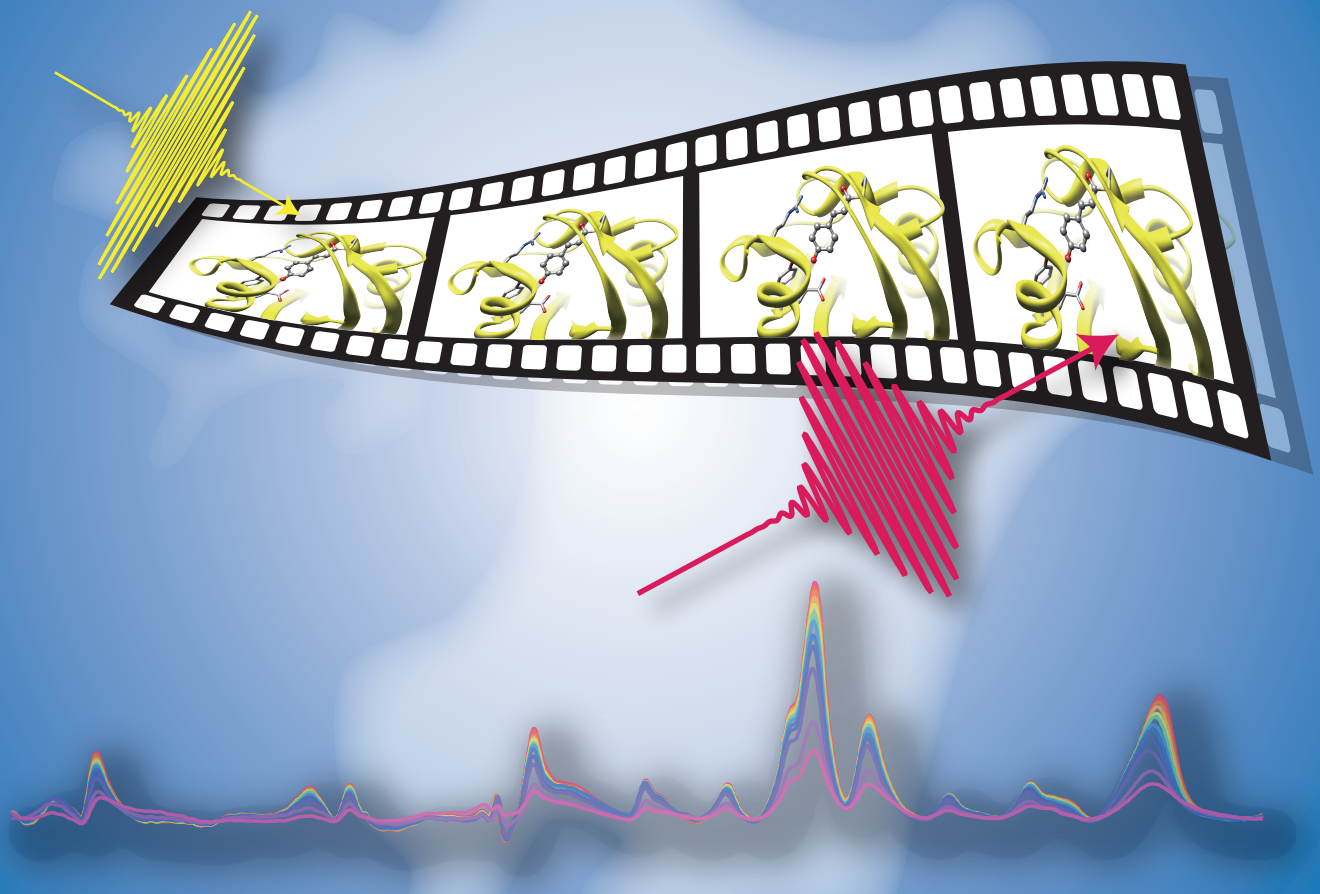
XVIth International Conference on Time-Resolved Vibrational Spectroscopy (TRVS 2013)



Beppu, Oita, Japan
May 19-24, 2013

TRVS 別府2013

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Time Table

Morning

	Sunday (May 19)	**Monday** (May 20)	**Tuesday** (May 21)	**Wednesday** (May 22)	**Thursday** (May 23)	**Friday** (May 24)
7:30		Breakfast	Breakfast	Breakfast	Breakfast	Breakfast
8:30		Opening Remark				
8:40		(Chair: Hamm) Elsaesser				
8:50			(Chair: Tahara) Shen	(Chair: Champion) Kim	(Chair: Elsaesser) Zinth	(Chair: Yoshizawa) Miller
9:00						
9:10						
9:20		(Chair: Tominaga) Khalil		Berg	Kennis	Iwata
9:30			(Chair: H. Noguchi) Bonn			
9:40				Break		Bakulin
9:50		Vöhringer			Kukura	
10:00			Nihonyanagi			Ashihara
10:10		Peng		(Chair: Heilweil) Zanni	Ishibashi	
10:20			Watanabe			Break
10:30		Break			Break	
10:40			Break	Mukamel		
10:50						
11:00						(Chair: Wynne) Tominaga
11:10		(Chair: Nibbering) Hamm		Kuroda	(Chair: Torii) Shirota	
11:20			(Chair: Gerwert) Champion			Heyne
11:30				Excursion (including lunch)	Wynne	
11:40		Ohta	Mizutani			Iwamura
11:50					Laage	
12:00		DiDonato	Meech			Ando
12:10						
12:20		Torii	Thor		Saito	Closing Remark
12:30						Lunch
12:40		Lunch	Lunch		Lunch	

Afternoon

	Sunday (May 19)	**Monday** (May 20)	**Tuesday** (May 21)	**Wednesday** (May 22)	**Thursday** (May 23)	**Friday** (May 24)
14:00	Arrival Registration	(Chair: Simpson) Cerullo	(Chair: Takeuchi) Ernsting	Excursion (including lunch)	(Chair: Mizutani) T. Noguchi	Departure
14:10						
14:20						
14:30		Kobayashi	McCamant		Kandori	
14:40						
14:50		Joo	Scopigno		Heberle	
15:00						
15:10		Ruhman	Yoshizawa			
15:20					Break	
15:30			Break			
15:40		Break			(Chair: Meech) Gerwert	
15:50						
16:00						
16:10			(Chair: Mukamel) Takaya		Nibbering	
16:20		(Chair: Yamaguchi) Fujii				
16:30			Shigeto		Pshenichnikov	
16:40						
16:50		Ebata	Fischer		George	
17:00						
17:10		Lee	Tanimura			
17:20						
17:30		Sekiya	Yagi		Presentation of Poster Award	
17:40						
17:50						
18:00	Reception	Dinner	Dinner		Free night	
19:00				Banquet		
20:00		Poster 1	Poster 2			
21:00						
22:00						

Conference Program

Monday May 20

8:30 Opening Remark

Chairperson: Peter Hamm (University of Zurich, Switzerland)

8:40 PL1 Ultrafast 2D infrared spectroscopy of phosphate-water interactions and water dynamics in phospholipid reverse micelles
René Costard, Ismael A. Heisler, Christian Greve, and **Thomas Elsaesser**

Chairperson: Keisuke Tominaga (Kobe University, Japan)

9:20 IT1 The role of high frequency vibrations in ultrafast metal-to-metal charge transfer transitions in mixed valence complexes
Michael S. Lynch, Karla M. Slenkamp, Benjamin E. Van Kuiken, Mark Cheng, Stephanie L. Daifuku, Caitlin Bannan, and **Munira Khalil**

9:50 CT1 A hydrogen-bond "flip-flop" through a Bjerrum-type defect
Martin Olschewski, Jörg Lindner, and **Peter Vöhringer**

10:10 CT2 Nanosecond tautomerization dynamics of aromatic heterocycles studied by temperature-jump transient 2D IR spectroscopy: application to an anti-HIV drug
Chunte Sam Peng, Carlos R. Baiz, Mike Reppert, Vipender Singh, Deyu Li, Tiffany J. Amariuta, John M. Essigmann, and Andrei Tokmakoff

10:30 Coffee Break

Chairperson: Erik T.J. Nibbering (Max Born Institute, Germany)

11:10 IT2 Water Friction Dominates Dynamics of a Photoswitchable Allosteric Protein
Brigitte Buchli, Steven A. Waldauer, Reto Walser, Rolf Pfister, Oliver Zerbe, and **Peter Hamm**

11:40 CT3 Accessing solute-solvent interactions and solvation dynamics with small ionic probes: Ultrafast infrared spectroscopic study
Kaoru Ohta, Kyoko Aikawa, and Keisuke Tominaga

12:00 CT4 Ultrafast Vis-Pump/IR-Probe and Transient 2D-IR Investigation of the Excited State Dynamics of trans-β-apo-8'-carotenal
Mariangela Di Donato, Andrea Lapini, Manuela Lima, Roberto Righini, Chiara Cappelli, Fabrizio Santoro, Mireia Segado, and Francisco Jose Avila Ferrer

12:20 CT5 Band merger and intensity bias in 1D and 2D vibrational spectra arising from coupling between different isotopic species
Hajime Torii, Maria Grazia Giorgini, and Maurizio Musso

12:40 Lunch

Chairperson: Cather Simpson (The University of Auckland, New Zealand)

14:00 IT3 Real-time wavepacket dynamics through a conical intersection
Giulio Cerullo, Dario Polli, Marco Garavelli, and Richard Mathies

14:30 CT6 Time-resolved spectroscopy of J-aggregates with sub-10-fs resolution
Takayoshi Kobayashi, Daisuke Hasegawa, Kazuaki Nakata, Eiji Tokunaga, Okamura Kotaro, and Du Juan

14:50 CT7 Excited state intramolecular proton transfer dynamics of hydroxyanthraquinones in solution by impulsive excitation of vibrations
Myeongkee Park, Jaehyun Ryu, and **Taiha Joo**

15:10 IT4 Following excited state evolution with impulsive vibrational spectroscopy
A. Wand and **Sanford Ruhman**

15:40 Coffee Break

Chairperson: Shoichi Yamaguchi (RIKEN, Japan)

16:20 IT5 Water migration dynamics studied by picosecond time-resolved IR spectroscopy
Masaaki Fujii

16:50 CT8 Study on photoisomerization of PYP chromophore by picosecond time-resolved pump-probe spectroscopy in the gas phase
Takayuki Ebata, Yasunori Miyazaki, Daiki Shimada, Yoshiya Inokuchi, and Masahiro Ehara

17:10 CT9 Effects of Hydrogen Bonding on Internal Conversion of GFP-like Chromophores
Chi-Wen Cheng, Guan-Jhih Huang, Hung-Yu Hsu, Ch. Prabhakar, Eric Wei-Guang Diau, Jye-Shane Yang, and **Yuan-Pern Lee**

17:30 CT10 Excited-state multiple proton transfer in solvated 7-azaindole clusters
Kenji Sakota, Yuto Ikegami, and **Hiroshi Sekiya**

18:00 Dinner

20:00 Poster Session 1 (PA1-PA43)

Tuesday May 21

Chairperson: Tahei Tahara (RIKEN, Japan)

8:50 PL2 Studies of Organic Monolayers at Water interfaces
Shuai Zha, Shanshan Yang, Yu-Chieh Wen, Chuanshan Tian, and **Y. Ron Shen**

Chairperson: Hidenori Noguchi (National Institute for Materials Science, Japan)

9:30 IT6 Vibrational and reorientational dynamics of interfacial water
Cho-Shuen Hsieh, Masanari Okuno, R. Kramer Campen, Ellen H.G. Backus, Huib J. Bakker, and **Mischa Bonn**

10:00 CT11 2D Heterodyne-Detected VSFG Spectroscopy of Water at Aqueous Interfaces
Satoshi Nihonyanagi, Prashant C. Singh, Shoichi Yamaguchi, and Tahei Tahara

10:20 CT12 Vibrational dynamics of adsorbates on metal surfaces studied by time-resolved sum-frequency generation
Kazuya Watanabe, Ken-ichi Inoue, Yoshiki Miyamoto, Toshiki Sugimoto, and Yoshiyasu Matsumoto

10:40 Coffee Break

Chairperson: Klaus Gerwert (Ruhr-University Bochum, Germany)

11:20 CT13 Heme cyanide photodissociation in myoglobin and horseradish peroxidase
Weiqiao Zeng, Yuhan Sun, Abdelkrim Benabbas, and **Paul M. Champion**

11:40 CT14 Allosteric dynamics of hemoglobin revealed by time-resolved resonance Raman spectroscopy
Yasuhisa Mizutani, Kenta Yamada, Haruto Ishikawa, and Misao Mizuno

12:00 CT15 Proteins in Action: Time Resolved Infra-red Study of a Photoactive Flavoprotein from Femtoseconds to Milliseconds
Richard Brust, Andras Lukacs, Allison Haigney, Kiri Addison, Agnieszka Zieba, Michael Towrie, Gregory M. Greetham, Peter J. Tonge, and **Stephen R. Meech**

12:20 CT16 Proton transfer and photoswitching in Fluorescent Proteins
Jasper J. van Thor, Marius Kaucikas, Paul Champion, and J. Timothy Sage

12:40 Lunch

Chairperson: Satoshi Takeuchi (RIKEN, Japan)

14:00 IT7 Femtosecond stimulated Raman scattering of S_1 *trans*-and *cis* stilbene
Sergey A. Kovalenko, Alexander L. Dobryakov, and **Nikolaus P. Ernsting**

14:30 CT17 Vibrational Relaxation of Guanosine Following Ultraviolet Photoexcitation
David W. McCamant, J. Reddy Challa, Joohyun Lee, and Yong Du

14:50 CT18 Sub-ps photoinduced dynamics in Heme-proteins studied by Femtosecond Stimulated Resonance Raman Scattering
Emanuele Pontecorvo, Carino Ferrante, and **Tullio Scopigno**

15:10 CT19 Difference of the carotenoid S* state between light harvesting complex and solution revealed by femtosecond stimulated Raman spectroscopy
Masayuki Yoshizawa, Orihiro Yoshimatsu, Kenta Abe, Shunsuke Sakai, Tomoko Horibe, Ritsuko Fujii, Mamoru Nango, and Hideki Hashimoto

15:30 Coffee Break

Chairperson: Shaul Mukamel (University of California, Irvine, USA)

16:10 CT20 Femtosecond near-IR multiplex stimulated Raman gain and loss spectroscopy of β-carotene in 1.0 – 1.6μm region
Tomohisa Takaya and Koichi Iwata

16:30 CT21 New insights into the reactivity, ordering, and structure of the low-lying excited triplet states of aromatic compounds as provided by time-resolved near/mid-IR spectroscopy
Sohshi Yabumoto, Sudhakar Narra, Hiro-o Hamaguchi, and **Shinsuke Shigeto**

16:50 CT22 Electronic and vibrational coherence during the initial charge separation in Photosynthesis
Sighart F. Fischer, Philipp O. J. Scherer, and Wolfgang Dietz

17:10 CT23 Water Potential for Vibrational Spectroscopy
Yoshitaka Tanimura, Taisuke Hasegawa, and Hironobu Ito

17:30 CT24 Anharmonic vibrational structure calculations from the first-principles
Kiyoshi Yagi

18:00 Dinner

20:00 Poster Session 2 (PB1-PB43)

Wednesday May 22

Chairperson: Paul Champion (Northeastern University, U.S.A.)

8:50 IT8 Exciton Delocalization Processes of Various π-Expanded Oligothiophenes
Dongho Kim

9:20 CT25 Vibrational energy transport through molecules
Christopher M. Berg, Brant Pein, Yuxiao Sun, and Dana D. Dlott

9:40 Coffee Break

～Robin M. Hochstrasser's Memorial Session～

Chairperson: Edwin Heilweil (National Institute of Standards & Technology, U.S.A.)

10:10 IT9 Quantifying transition dipole strengths to identify molecular structures
Martin T. Zanni

10:40 IT10 Monitoring excited-state vibrational dynamics by broadband infrared or Raman probes; A unified picture based on loop diagrams
Konstantin E. Dorman, Benjamin P. Fingerhut, and **Shaul Mukamel**

11:10 CT26 Structure and dynamics of a drug bound to its allosteric pocket in HIV-1 reverse transcriptase
Daniel Kuroda, J. Reddy Challa, Thomas Troxler, Joseph D. Bauman, Disha Patel, Kalyan Das, Eddy Arnold, and Robin M. Hochstrasser

Thursday May 23

Chairperson: Thomas Elsaesser (Max born Institute, Germany)

8:50 IT11 Light-triggered peptides – a new tool for the investigation of ultrafast folding dynamics
Wolfgang Zinth(TRVS2013 awardee), Andreas Deeg, Michael Rampp, and Bert Pilles

9:20 IT12 Improving signal generation and collection in Femtosecond Stimulated Raman Spectroscopy
John T.M. Kennis and Miroslav Kloz

9:50 CT27 Revealing excited state nuclear coherence in the photoisomerisation of bacteriorhodopsin by population assisted impulsive Raman
Matz Liebel and **Philipp Kukura**

10:10 CT28 Time-resolved IR spectroscopy of cyclopentane-1,3-diyl biradicals
Taka-aki Ishibashi, Akihiro Maeda, Takahide Oshita, and Manabu Abe

10:30 Coffee Break

Chaiperson: Hajime Torii (Shizuoka University, Japan)

11:10 CT29 Probing Dimerization of 7-Azaindole in Solutions by Femtosecond Raman-Induced Kerr Effect Spectroscopy
Hideaki Shirota, Takao Fukuda, and Tatsuya Kato

11:30 CT30 Like-charge ion pairing in aqueous guanidinium chloride solution addressed by ultrafast optical Kerr-effect (OKE) spectroscopy
David Turton and **Klaas Wynne**

11:50 IT13 When do ions accelerate or retard water dynamics?
Guillaume Stirnemann, Erik Wernersson, Pavel Jungwirth, and **Damien Laage**

12:20 CT31 Hydrogen bond dynamics in supercooled water: Frequency dependent specific heat and emergence of correlated dynamics
Shinji Saito, Iwao Ohmine, and Biman Bagchi

12:40 Lunch

Chairperson: Yasuhisa Mizutani (Osaka University, Japan)

14:00 IT14 Mechanism of photosynthetic water oxidation as studied by flash-induced FTIR difference and time-resolved IR spectroscopies
Takumi Noguchi

14:30 CT32 Mechanism of light-driven sodium ion pump
Hideki Kandori, Hui-Fen Chen, and Keiichi Inoue

14:50 IT15 Proton transfer reactions and structural changes of the optogenetic protein channelrhodopsin-2 traced by time-resolved step-scan FTIR spectroscopy
V.A. Lórenz-Fonfría, T. Resler, N. Krause, M. Nack, M. Gossing, G. Fischer von Mollard, C. Bamann, E. Bamberg, R. Schlesinger, **Joachim Heberle**

15:20 Coffee Break

Chairperson: Stephen Meech (University of East Anglia, UK)

15:50 IT16 Catalysis of small GTPases by their G-Activating Proteins (GAPs) analyzed by time-resolved FTIR spectroscopy
Klaus Gerwert

16:20 CT33 Ultrafast Dynamics of Specific Interactions in Photoacid-Base Complexes
M. Prémont-Schwarz, D. Xiao, S. Keinan, D. Pines, D. Huppert, E. Pines, V.S. Batista, and **Erik T.J. Nibbering**

16:40 CT34 Ultrafast Charge Generation in Novel Push –Pull Polymers
Vlad G. Pavelyev, Almis Serbenta, Stoichko D. Dimitrov, James R. Durrant, Paul H.M. van Loosdrecht, and **Maxim S. Pshenichnikov**

17:00 IT17 Probing Organometallic Photochemistry in Conventional and supercritical Fluids using time-resolved IR
Michael George

17:30 Presentation of Poster Award

Friday May 24

Chairperson: Masayuki Yoshizawa (Tohoku University, Japan)

8:50 IT18 "Making the Molecular Movie": Direct Observation of Atomic Motions Involved in Mode Coupling Along Reaction Coordinates
R.J. Dwayne Miller

9:20 CT35 Energy transfer in phosphatidylcholine lipid bilayer membranes examined by picosecond time-resolved Raman spectroscopy
Yuki Nojima, Tomohisa Takaya, and **Koichi Iwata**

9:40 CT36 Dynamics of molecular systems probed by IR-induced conductivity
Artem A. Bakulin, Akshay Rao, Robert Lovrincic, Maxim S. Pshenichnikov, Huib J. Bakker, David Cahen, and Richard H. Friend

10:00 CT37 Control of multipath interference in vibrational excitations for anharmonically coupled oscillator systems
Satoshi Ashihara and Jumpei Tayama

10:20 Coffee Break

Chairperson: Klaas Wynne (University of Glasgow, UK)

11:00 CT38 Vibrational dynamics in the electronically excited state in hydrogen bonding solvents
Yuki Fukui, Minako Kondo, Kaoru Ohta, and **Keisuke Tominaga**

11:20 CT39 Ultrafast photoisomerization of Pfr phytochrome studied by time-resolved infrared and Raman spectroscopy
Karsten Heyne, Yang Yang, Peter Schmieder, Clark Lagarias, Richard A. Mathies, and Jyothisman Dasgupta

11:40 CT40 Inter-molecular Coherent Vibration in Oligomers of Gold(I) complex
Munetaka Iwamura, Koichi Nozaki, Satoshi Takeuchi, and Tahei Tahara

12:00 CT41 Semiquantal wave packet molecular dynamics simulation of hydrogen-bond dynamics in water
Koji Ando, Junichi Ono, and Kim Hyeon-Deuk

12:20 Closing Remark

Poster Session 1 (PA1-PA43)　20:00～ Monday May 20

PA1 New Methods in Mixed Electronic-Vibrational Coherent Multidimensional Spectroscopy: Triple Sum Frequency CMDS and Application

Erin S. Boyle, Andrei V. Pakoulev, and John C. Wright

PA2 Early steps in the uncaging reaction of NVOC protected puromycin

Jörg Kohl-Landgraf, Florian Buhr, Harald Schwalbe, and Josef Wachtveitl

PA3 Mutual Orientation of Reactants in Bimolecular Photoinduced Electron Transfer in Solution

Marius Koch and Eric Vauthey

PA4 UV-excited time-resolved HD-VSFG study of the photoionization dynamics of indole at the air/water interface: A vibrational signature of hydrated electrons at the interface

Korenobu Matsuzaki, Satoshi Nihonyanagi, Shoichi Yamaguchi, Takashi Nagata, and Tahei Tahara

PA5 New Methods to Measure Anharmonic Coupling using Femtosecond Stimulated Raman Spectroscopy

Barbara Dunlap, Peter Richter, and David W. McCamant

PA6 Conformational change of azobenzene-based photoswitchable OmPE-foldamer due to photoisomerization

Sabrina Steinwand, Chavdar Slavov, Zhilin Yu, Stefan Hecht, and Josef Wachtveitl

PA7 Raman-enhancement mechanism by a nearby plasmonic cluster: the coupling of plasmonic electron motion with vibrational modes of analyte

Tomokazu Yasuike and Katsuyuki Nobusada

PA8 Charge Dynamics in Novel Star-Shaped Conjugated Molecules

Oleg V. Kozlov, Vlad G. Pavelyev, Almis Serbenta, Yuriy N. Luponosov, Sergei A. Ponomarenko, Dmitry Yu. Paraschuk, Andreas Elschner, and Maxim S. Pshenichnikov

PA9 Femtosecond Time-Domain Raman Tracking of the Primary Photoreaction Process of Photoactive Yellow Protein

Hikaru Kuramochi, Satoshi Takeuchi, Hironari Kamikubo, Mikio Kataoka, and Tahei

Tahara

PA10 Real-Time Tracking of Two Phytochrome Isoforms During Pr Photoisomerization

Y. Yang, M. Linke, T. von Haimberger, J. Hahn, P. Schmieder, R. Matute, L. González, K. Heyne

PA11 Salt bridges function as nucleation sites for α-helix folding

Heleen Meuzelaar, Martijn Tros, Adriana Huerta Viga, Chris N. van Dijk, and Sander Woutersen

PA12 Towards Time-Resolved Host-Guest Chemistry: Charge Transfer Dynamics of Perylene-Macrocycle Complex

Ryan M. Young, Scott M. Dyar, Dick T. Co, and Michael R. Wasielewski

PA13 Structural transformations of liquid water under high pressure conditions: experimental and computational characterization

Andrea Lapini, Samuele Fanetti, Marco Pagliai, Mariangela di Donato, Margherita Citroni, Sandro Scandolo, Roberto Bini, and Roberto Righini

PA14 Mid-infrared spectroscopy by chirped pulse upconversion

Jingyi Zhu, Tilo Mathes, John T.M. Kennis, and Marie Louise Groot

PA15 Conformational dynamics of fish type III antifreeze protein studied with time-resolved vibrational spectroscopy

Stephan Lotze and Huib J. Bakker

PA16 Visible pump-IR probe Spectroscopy on Fluorenone and Water-soluble Fluorenone in Solutions

Yuki Fukui, Minako Kondo, Kaoru Ohta, and Keisuke Tominaga

PA17 Laser-induced temperature-jump infrared-spectroscopy to study peptide folding dynamics with site-specific resolution

Karin Hauser, Alexander Popp, and Benjamin Heck

PA18 Transporting a proton with a molecular crane

Tibert H. vab der Loop, Freek Ruesink, Hans J. Sanders, Wybren J. Buma, and Sander Woutersen

PA19 Triplet Formation Mechanism in Cofacial Perylene Diimide Dimers Interrogated by Femtosecond Stimulated Raman Spectroscopy

Kristen E. Brown, Kelly M. Lefler, Walter A. Salamant, Dick T. Co, and Michael R. Wasielewski

PA20 S_2 Fluorescence Dynamics of *meso*-Aryl-substituted Subporphyrins

Jooyoung Sung, Pyosang Kim, Shun Saga, Atsuhiro Osuka, and Dongho Kim

PA21 Ultrafast dynamics of solvent coordination to organometallic photoproducts probed via solvent vibrational oscillators

Son C. Nguyen, Justin P. Lomont, Ben W. Caplins, and Charles B. Harris

PA22 Bimolecular Electron Transfer between Pyrene and 1,4-Dicyanobenzene as Studied by Nanosecond Time-Resolved Near/Mid-Infrared Spectroscopy

Sudhakar Narra and Shinsuke Shigeto

PA23 Two-dimensional broadband mid-IR spectroscopy

Mark Cheng, Anthony Reynolds, and **Munira Khalil**

PA24 Femtosecond OPA pumped by 1030 nm Yb:KGW laser

Valeri Kozich, M. Hartmann, and K. Heyne

PA25 Analyzing brominated Al-Corroles with Vis-pump and IR-, NIR- and VIS- probe experiments

Till Stensitzki, Yang Yang, T. von Haimberger, Atif Mahammed, Zeev Gross, and Karsten Heyne

PA26 Initial interfacial structure and dynamics of dye sensitizer under photo-excitation studied by ultrafast infrared spectroscopy

Hidenori Noguchi, Mikio Ito, and Kohei Uosaki

PA27 Elucidating the mechanism of a unidirectional molecular motor

Saeed Amirjalayer, Wesley R. Browne, Ben L. Feringa, Wybren J. Buma, and Sander Woutersen

PA28 Towards excited-state surface-enhanced femtosecond stimulated Raman spectroscopy

Natalie L. Gruenke, Renee R. Frontiera, and Richard P. Van Duyne

PA29 Folding of a light-switched β-hairpin peptide: Comparison of isomerization and temperature-jump induced peptide dynamics

Andreas Deeg, Michael Rampp, Alexander Popp, Bert Pilles, Tobias Schrader, Jose Pfizer, Luis Moroder, Karin Hauser, and Wolfgang Zinth

PA30 Links between Structure, Dynamics and Function in the Inhibition of Catalase by Nitric Oxide

Marco Candelaresi, Andrea Gumiero, **Katrin Adamczyk**, Kristy Robb, Cesar Bellota-Antón, Vartul Sangal, John Munnoch, Gregory M. Greetham, Michael Towrie, Paul A. Hoskisson, Anthony W. Parker, Nicholas P. Tucker, Martin A. Walsh, and Neil T. Hunt

PA31 Secondary and quaternary structural imaging of human hairs by using VSFG-detected IR super-resolution microscope

Makoto Sakai and Masaaki Fujii

PA32 Dynamics of two-photon isomerization of DTTCI observed by femtosecond pump-probe and two-pulse correlation measurements

Koich Furuta, Masanori Fuyuki, and **Akihide Wada**

PA33 Ultrafast hydrogen-bonding dynamics in the electronic excited state of photoactive yellow protein

Ryosuke Nakamura, Norio Hamada, Kenta Abe, and Masayuki Yoshizawa

PA34 Time-resolved IR spectroscopy of hydrogenase enzyme mimics: the effect of hydrogel encapsulation

Pim W.J.M. Frederix, Rafal Kania, Joseph A. Wright, Rein V. Ulijn, Christopher J. Pickett, and Neil T. Hunt

PA35 Real-time observation of destruction of hydration shells

Akira Yamakata and Masatoshi Osawa

PA36 Time-resolved FTIR study of a light-driven sodium pump rhodopsin

Hui-Fen Chen, Keiichi Inoue, and Kandori Hideki

PA37 Towards time-domain ultrafast vibrational spectroscopy of chemical reaction dynamics
Matz Liebel and Philipp Kukura

PA38 Bimodal dynamics of DNA bubbles
Chris N. van Dijk, Heleen Meuzelaar Matthijs R. Panman, and Sander Woutersen

PA39 Determination of Huang-Rhys factors of multi-dimensional hyper-potential surfaces obtained by a few-cycle pulse laser
Takayoshi Kobayashi, Tsugumasa Iiyama, Kotaro Okamura, Juan Du, and Toshio Masuda

PA40 Ultrafast time-resolved pump/IR probe spectroscopy of [FeFe]-hydrogenase model compounds
Melissa Johnson, James Thuman, Christopher J. Stromberg, and **Edwin J. Heilweil**

PA41 Spectral diffusion of heavy water in presence of bromide and iodide ions at supercritical conditions: First principle molecular dynamics study
Anwesa Karmakar and Amalendu Chandra

PA42 Anomalous Blinking Characteristics in Single Molecule Surface-Enhanced Raman Spectroscopy (SMSERS)
Wen-Hsiang Yu and Chao-Yi Tai

PA43 Intermolecular vibrational energy transfer analyzed by ultrafast two-dimensional infrared spectroscopy
Albert A. Villaeys and **Kuo Kan Liang**

Poster Session 2 (PB1-PB43) 20:00~ Tuesday May 21

PB1 Anharmonic and solvent effects on Franck-Condon factors with application to molecular electronic spectroscopy
Chaoyuan Zhu and Sheng Hsien Lin

PB2 Ultrafast isomerization dynamics of a substituted azobenzene driving a cyclodextrin shuttle
Matthew M. Sartin, Masahisa Osawa, and Tahei Tahara

PB3 Femtosecond stimulated Raman spectroscopy of a BLUF protein PapB from the purple bacterium *Rhodopseudomonas palustris*

Tomotsumi Fujisawa, Satoshi Takeuchi, Shinji Masuda, and Tahei Tahara

PB4 Two-dimensional heterodyne-detected vibrational sum frequency generation spectroscopy of water at a charged interface with excess salt

Prashant C. Singh, Satoshi Nihonyanagi, Shoichi Yamaguchi, and Tahei Tahara

PB5 Fullerene Excitons Reveal Morphology of Polymer: Fullerene Blends

Almis Serbenta, Vlad G. Pavelyev, Jan C. Hummelen, Paul H.M. van Loosdrecht, and Maxim S. Pshenichnikov

PB6 Three dimensional infrared spectroscopy of ice Ih

Fivos Perakis, Joanna Borek, and Peter Hamm

PB7 Parallel Relaxation Pathways of Malachite Green Revealed by Ultrafast Pump-Dump-Probe Spectroscopy

Zhengrong Wei, Satoshi Takeuchi, and Tahei Tahara

PB8 *In situ* monitoring of a protein folding process on the artificial lipid bilayer by Surface Enhanced Infrared Absorption Spectroscopy

Kenichi Ataka, Axel Baumann, Silke Kerruth, Ramona Schlesinger, Jörg Fitter, and Joachim Heberle

PB9 Chemical exchange between phenol and phenol-benzene complex observed by 3D IR spectroscopy

Joanna A. Borek, Fivos Perakis, and Peter Hamm

PB10 Ligand Binding Studied by 2D IR Spectroscopy Using the Azidohomoalanine Label

Robbert Bloem, **Klemens Koziol**, Steven A. Waldauer, Brigitte Buchli, Reto Walser, Brighton Samatanga, Ilian Jelesarov, and Peter Hamm

PB11 Quantum decoherence in vibrational nonadiabatic transitions of water studied by quantum-classical molecular dynamics simulations

Tatsuya Joutsuka, Ward H. Thompson, and Damien Laage

PB12 Two-Dimensional Raman-THz Spectroscopy of Water

Janne Savolainen, Saima Ahmed, and Peter Hamm

PB13 Ultrafast dynamics of excited state DNA probed by femtosecond stimulated Raman spectroscopy

Joohyun Lee, J. Reddy Challa, Yong Du, and David W. McCamant

PB14 Excited state dynamics for thymine by using sub-10 femtosecond deep ultraviolet pump and probe pulses

Bing Xue, Takayoshi Kobayashi, Juan Du, and Yongliang Jiang

PB15 Picosecond protein response to the chromophore isomerization in microbial rhodopsins

Misao Mizuno, Seisuke Inada, Yumi Shimoo, Hideki Kandori, Yuki Sudo, and Yasuhisa Mizutani

PB16 Chromophore structures of photocycle intermediates in *Gloeobacter* rhodopsin: a resonance Raman study

Ayumi Nakajima, Misao Mizuno, Hideki Kandori, and Yasuhisa Mizutani

PB17 Ultrafast structural dynamics of membrane-bound water molecules revealed by two-dimensional surface-specific vibrational spectroscopy

Ellen H.G. Backus, Zhen Zhang, Lukasz Piatkowski, Huib J. Bakker, and Mischa Bonn

PB18 Vibrational-Excitation Induced Proton Transfer in Nafion Nano-Channels

Liyuan Liu, **Artem Bakulin**, and Huib J. Bakker

PB19 Towards unraveling the mechanism of an anti-tuberculosis drug target

Daniel J. Shaw, Katrin Adamczyk, Niall Simpson, Kirsty Robb, Marco Candelaresi, Pim W.J.M. Frederix, Gregory M Greetham, Michael Towrie Anthony W. Parker, Paul Hoskisson, and Neil T. Hunt

PB20 Theoretical study on frequency fluctuation and energy relaxation of HOH bend in liquid water

Sho Imoto and Shinji Saito

PB21 Thermochemical solar energy capture via photoisomerization of dimetallic fulvalene complexes

Justin Lomont, Son Nguyen, Zongrui Hou, Michael R. Harpham, Jeffrey C. Grossman,

Yosuke Kanai, Michael W. Mara, Andrew B. Stickrath, Alexie M. Kolpak, Donghwa Lee, Di-Jia Liu, Kasper Moth-Poulsen, Nickolai Vinokurov, Lin X. Chen, K. Peter C. Vollhardt, and Charles B. Harris

PB22 Exciton Delocalization and Dynamics in Helical π-stacks of Self-assembled Perylene Bisimides

Jong Min Lim, Pyosang Kim, Frank Würthner, and Dongho Kim,

PB23 Relationship Between Exciton Delocalization and Excited-State Conformational Dynamics in Linear and Cyclic π-Conjugated Oligothiophenes

Pyosang Kim, Jaesung Yang, Masahiko Iyoda, and Dongho Kim

PB24 Vibrational Relaxation in RNA Nucleotides following Electronic Excitation

Jakob B. Nielsen, Jan Thøgersen, Svend K. Jensen, and Søren R. Keiding

PB25 Vibronic relaxation dynamics in multiphoton reactions of indocyanine green in ethanol

Masanori Fuyuki and Akihide Wada

PB26 The influence of hybrid orbital reconstruction on the mechanism of proton transfer in protonated benzene

Ayaka Kuroki, Hiroshi Ushiyama, and Koichi Yamashita

PB27 Water migration around peptide linkage in Acetanilide-(water) 1:1 cluster studied by time-resolved IR spectroscopy

Martin Weiler, Mitsuhiko Miyazaki, Hiroshi Sekiya, Otto Dopfer, and Masaaki Fujii

PB28 Dispersed three pulse vibrational photon echoes of N_2O in water and octanol: Model systems for phospholipids

Jeffrey T. Shattuck, Shyam Erramilli, and Lawrence D. Ziegler

PB29 Molecular dynamics simulation for fast dielectric relaxation of hydrated ion

Yoji Kubota, Akira Yoshimori, Nobuyuki Matsubayashi, Makoto Suzuki, and Ryo Akiyama

PB30 VIPER 2D-IR: chemical exchange beyond the vibrational lifetime and sub-ensemble selective photochemistry

Luuk J.G.W. van Wilderen, Andreas T. Messmer, and Jens Bredenbeck

PB31 Time resolved IR spectroscopy on the excited state decay in single stranded DNA

Dominik B. Bucher, Bert Pilles, and Wolfgang Zinth

PB32 Determining in situ protein conformation and orientation from the amide-I sum-frequency generation spectrum: theory and experiment

Steven J. Roeters, Mischa Bonn, and Sander Woutersen

PB33 Effect of specific interaction on C=O vibrational dynamics of the excited state 4-Aminopthalimide

Minako Kondo, Kaoru Ohta, and Keisuke Tominaga

PB34 Comparison of vibrational dynamics between hydrophobic probe and ionic probe in water studied by two-dimensional infrared spectroscopy

Masaki Okuda, Kaoru Ohta, and Keisuke Tominaga

PB35 Structure and Dynamics of Aqueous Hydroxides Studied Using Ultrafast Broadband Infrared Spectroscopy

Aritra Mandal, Krupa Ramasesha, Luigi De Marco, and Andrei Tokmakoff

PB36 Ultrafast two-dimensional phase-resolved vibrational sum frequency spectroscopy of aqueous interfaces

Masanari Okuno, Cho-Shuen Hsieh, Ellen H.G. Backus, and Mischa Bonn

PB37 *Ab Initio* Study of $S_3 \rightarrow S_2$ and $S_2 \rightarrow S_1$ internal conversion of PRODAN molecule

Tomotaka Kunisada, Hiroshi Ushiyama, and Koichi Yamashita

PB38 Electrocyclization reaction of a photocromic molecular switch and excited state dynamics of the molecular constituents studied by Femtosecond Stimulated Resonance Raman Scattering

Emanuele Pontecorvo, Carino Ferrante, Christopher G. Elles, and Tullio Scopigno

PB39 2D IR spectroscopy with a phase-locked pulse pair delayed by a birefringent delay line

Julien Réhault, Margherita Maiuri, Daniele Brida, Cristian Manzoni, Jan Helbing, and Giulio Cerullo

PB40 Structural change and ligand discrimination of oxygen sensor protein FixL studied by ultraviolet resonance Raman spectroscopy

Takeo Yamawaki, Shinji Yano, Haruto Ishikawa, Misao Mizuno, Hiro Nakamura, Yoshitsugu Shiro, and Yasuhisa Mizutani

PB41 N-H Stretching Excitations in Adenosine-Thymidine Base Pairs in Solution: Pair Geometries, Infrared Line Shapes, and Ultrafast Vibrational Dynamics

C. Greve, N.K. Preketes, B. Koeppe, H. Fidder, R. Costard, I.A. Heisler, P.M. Tolstoy, F. Temps, S. Mukamel, T. Elsaesser, and **Erik.T.J. Nibbering**

PB42 Molecular dynamics of proteins in solutions studied by ultrafast Optical Kerr effect (OKE) spectroscopy

David Turton, Thomas Harwood, Hans Senn, Adrian Lapthorn, Elizabeth M. Ellis, and **Klaas Wynne**

PB43 Vibrational relaxation dynamics of the pseudohalide (PS) complexes $Ru(bpy)_2(PS)_2$, PS=CN, NCS and N_3

Ryan Compton Helen K. Gerardi, Daniel Weidinger, Douglas J. Brown, Walter J. Dressick, **Edwin J. Heilweil**, and Jeffrey C. Owrutsky

Oral Presentation
Monday

PL1

Ultrafast 2D infrared spectroscopy of phosphate-water interactions and water dynamics in phospholipid reverse micelles

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Phosphate-water interactions play a key role for the structural and functional properties of biomolecular systems such as phospholipid membranes and DNA. Nonlinear vibrational spectroscopy in the femtosecond time domain allows for mapping fluctuating interactions of hydrated phosphate groups and for unraveling the time scale and pathways of vibrational relaxation. Here, we study such processes in DOPC (dioleoylphosphatidylcholine) reverse micelles [1], a phospholipid model system containing small H_2O pools of variable size.

We report the first 2D spectra of phosphate stretching vibrations and other phospholipid modes in the frequency range from 1000 to 1300 cm^{-1}. The symmetric and asymmetric $(PO_2)^-$ stretch peaks display a pronounced inhomogeneous broadening that persists into the picosecond time domain. The off-diagonal width of the asymmetric stretch peak suggests that population relaxation with a 300 fs lifetime represents the predominant dephasing mechanism for water pools up to a 16:1 ratio of water to DOPC molecules (w_0=16). The 2D spectra also display a rich coupling scheme of phosphate and other vibrations in this frequency range.

In a second series of 2D experiments, we studied the dynamics of OH stretching excitations of the H_2O pool [2]. Average OH stretching lifetimes between 550 and 300 fs are found between w_0=1 and 16, and coupling to the OH bending mode is identified as the main decay channel. Such vibrational relaxation establishes a hot water ground state with a blue-shifted OH stretching absorption that displays a homogeneous lineshape and strongly affects the 2D spectra in a wide frequency range. An analysis of center line slopes shows that energy dissipation is substantially faster than structural fluctuations of the water pools for w_0=1 to 8. Our results suggest that local pools as small as 3 water molecules interacting with a phosphate head group are sufficient to establish a hot water ground state.

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The role of high frequency vibrations in ultrafast metal-to-metal charge transfer transitions in mixed valence complexes

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Transition metal mixed valence compounds serve as excellent model systems for probing coupled electronic and vibrational motions during ultrafast charge transfer processes. We have used two-dimensional infrared (2DIR) and IR pump-probe spectroscopies of coupled cyanide stretching frequencies to probe the ground electronic state of the mixed valence compounds $[(CN)_5Fe^{II}CNRu^{III}(NH_3)_5]^-$ (RuFe) and $[(CN)_5Fe^{II}–CN–Pt^{IV}(NH_3)_4–NC–Fe^{II}(CN)_5]^{4–}$ ($Fe^{II}Pt^{IV}Fe^{II}$) in deuterated water and formamide. The IR experiments provide a detailed map of the vibrational anharmonic couplings and the inter and intramolecular vibrational energy transfer pathways between the four coupled C≡N stretches as a function of the solvent environment.

Upon excitation at 400 nm, a metal-to-metal charge transfer transition occurs in $Fe^{II}Pt^{IV}Fe^{II}$ dissolved in D_2O. This is followed by back electron transfer on a ~110 fs time scale and vibrational cooling of $Fe^{II}Pt^{IV}Fe^{II}$ on a 1–2 ps time scale.[1] We probe the coherent and incoherent vibrational relaxation dynamics following the charge transfer process using doubly-resonant fifth-order nonlinear visible–infrared spectroscopies.[2] Excess energy deposited into the C≡N stretching modes of the molecule is monitored as the photochemical reaction takes place, elucidating the role of non-equilibrium vibrational energy relaxation in charge transfer processes. We find that vibrational relaxation dynamics change significantly during the charge transfer process and that coherent oscillations along the vibrational waiting time differ from the ground state by 7 cm^{-1} in a time-dependent manner.[3] Our experiments suggest that the high-frequency vibrational motions of the molecule are both coherently and incoherently coupled to the electronic charge transfer process.

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A hydrogen-bond “flip-flop” through a Bjerrum-type defect

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Structural disorder, Bjerrum defects, and hydrogen-bond reversal (coined H-bond “flip-flop”) are intimately linked molecular dynamical phenomena that are of fundamental importance for the properties of H-bonded systems. They are implicated in maintaining a unidirectional proton conductivity of linear H-bonded chains and they are responsible for the ”zero-Kelvin” entropy of ice. Here, we employed two-dimensional infrared (2DIR) exchange spectroscopy to directly observe this flip-flop process in the time domain. As a model system we used the intramolecular H-bond of the vicinal diol, pinacol (cf. Fig 1). Its IR absorption spectrum in the OH-region features a frequency-upshifted band due to the free OH (the H-bond acceptor) and a downshifted band due to the bound OH (the H-bond donor). The 2DIR spectrum of pinacol at early delays shows absorptive and emissive diagonal peaks only. However, as the time delay is increased strong off-diagonal peaks appear. Further 2DIR data on pinacol isotopomers and their mixtures reveal that the cross peaks do not originate from vibrational energy transfer.

Density functional theory (DFT) suggests an alternative mechanism for excitation exchange between bound and free OH-groups, which involves a synchronous disrotatory torsional isomerization about the two CC─OH bonds thereby interchanging the H-bond donating and accepting character of the two hydroxyls. This H-bond “flip-flop” is facilitated by a Bjerrum-type *D*-defect in which the intramolecular non-covalent contact is occupied by two H-atoms at the same time. Nonlinear response function simulations of the 2DIR data yield an exchange rate of 1 / 2 ps, in good agreement with an *ab initio* rate derived from DFT / transition state theory.

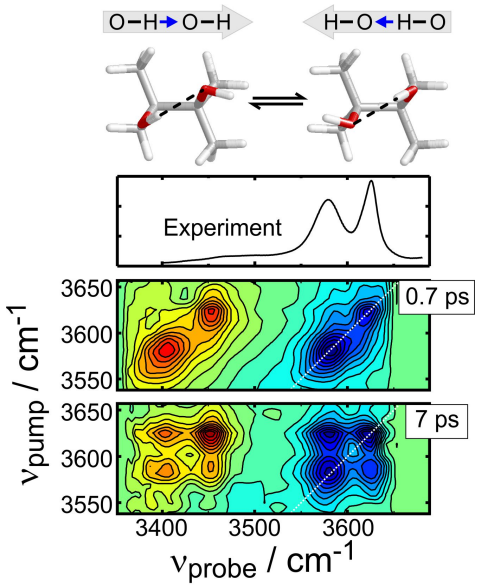

Fig. 1. Linear-IR and 2DIR spectra of pinacol in CCl4 at 298 K.

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Nanosecond tautomerization dynamics of aromatic heterocycles studied by temperature-jump transient 2D IR spectroscopy: application to an anti-HIV drug

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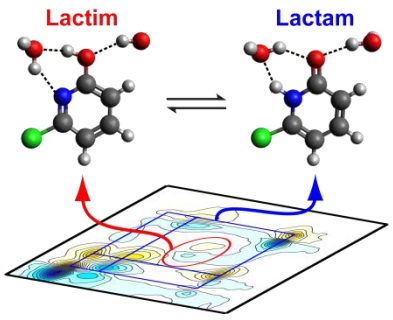
The tautomerism of aromatic heterocycles such as DNA bases has attracted considerable amount of interest because of its importance in many chemical and biological processes, such as ligand binding and enzyme catalysis. Moreover, it has been proposed that tautomerization of DNA bases can lead to spontaneous mutation. This concept, although has not been experimentally proved, has been utilized in some recent drug designs. It has been shown that by artificially introducing a deoxycytidine analogue called KP-1212 into the HIV genome, the viral population would eventually collapse due to elevated G to A mutations. It was hypothesized that the mutation originates from the tautomerization of KP-1212 from the canonical amino-keto form to the imino-keto form, which allows favorable hydrogen-bonding to adenine. In order to test this hypothesis, we first used 2D IR spectroscopy to characterize the tautomerism of a model system for studying DNA bases, pyridone derivatives, in aqueous solution under physiological conditions. The lactam and lactim tautomers were identified and distinguished by their distinctive cross-peak patterns. Furthermore, we performed transient temperature-jump (T-jump) 2D IR experiments to measure the nanosecond tautomerization kinetics of pyridone derivatives on the electronic ground-state. Finally, we applied this methodology to characterize the tautomeric equilibria of KP-1212 under physiological conditions. We identified significant enol tautomer population in addition to the proposed imino-keto tautomer. Using T-jump 2D IR spectroscopy, we observed nanosecond keto to enol tautomerization, which has profound implications on the mutation rate as the polymerase adds nucleotides to base-pair with KP-1212.



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Water Friction Dominates Dynamics of a Photoswitchable Allosteric Protein

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Allostery is a fundamental concept Nature uses to regulate the affinity of a certain substrate to an active site of a protein by binding a ligand to a distant allosteric site. Although there are many well-developed models of allosteric interactions and networks, little is known about the dynamics of allosteric conformational transitions on an atomistic level. In order to better understand the nature of the free energy landscape governing this dynamics, we cross-linked two amino acid side chains of the PDZ2 domain, a single-domain allosteric protein, with a photo-switchable azobenzene- moiety in a such a way that we can mimic the conformational transition upon ligand binding (Fig. 1a). Transient IR spectroscopy covering six orders of magnitudes in time is used to observe the protein response upon photo-initiation, which occurs in a highly non-exponential manner, stretching from picoseconds to 100's of nanoseconds (Fig. 1b). All-atom molecular dynamics (MD) simulations can reproduce that response quite well and furthermore suggests that this behavior reflects the friction of mostly the water surrounding the protein.

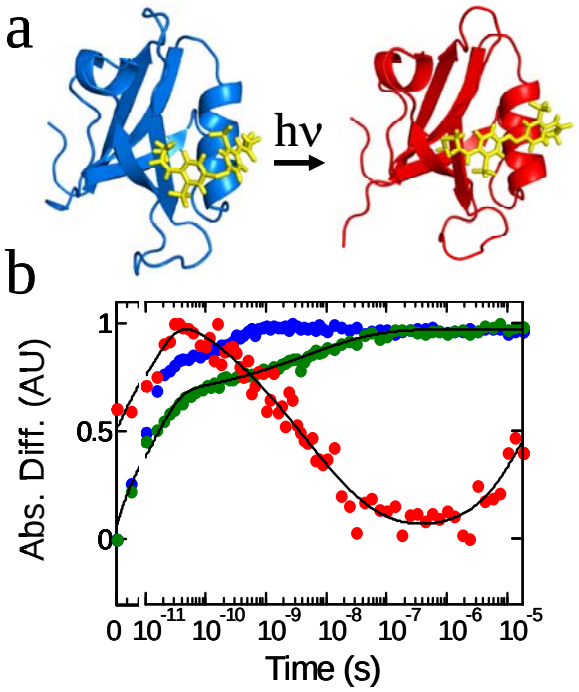

Fig. 1 (a) PDZ2 domain cross-linked by an azobenzene-moiety acting as photo- switch. (b) Transient IR response of the amide I band of the protein (red) and of a marker mode of the photo-switch (green). For comparison, the response of the same marker mode of the photo-switch not linked to the protein is shown as well.

Accessing solute-solvent interactions and solvation dynamics with small ionic probes: Ultrafast infrared spectroscopic study

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In the condensed phase, large molecular systems exhibit a complex potential energy landscape so that it is very difficult to obtain information on structural change and fluctuation of such systems on a fast time scale. It is known that azide and thiocyanate groups are excellent vibrational probes for studying the local interaction with the surrounding environment. Recently we studied the vibrational dynamics of the anti-symmetric stretching mode of small ions such as SCN^- and N_3^- in various polar solvents by using nonlinear infrared (IR) spectroscopy [1]. Our results showed that there exists a clear difference of the vibrational dynamics between protic and aprotic solvents. Hydrogen bonding interaction plays an important role in the structural fluctuations of the solution.

To order to understand molecular origin of the vibrational frequency fluctuation, we investigated the temperature dependence of the vibrational dynamics of the NO stretching mode of $[RuCl_5(NO)]^{2-}$ in water. In this work, we used 2D-IR spectroscopy to probe the spectral diffusion processes and extract the frequency-frequency correlation function. Figure 1 displays the example of 2D-IR spectrum in D_2O taken at 283 K and decay profiles of center line slope (CLS) calculated from 2D spectra. CLS decay is faster with increasing temperature. In this contribution, we will discuss comparison of the temperature dependence between frequency fluctuation and other dynamical quantities such as vibrational population relaxation and the reorientational dynamics in detail.

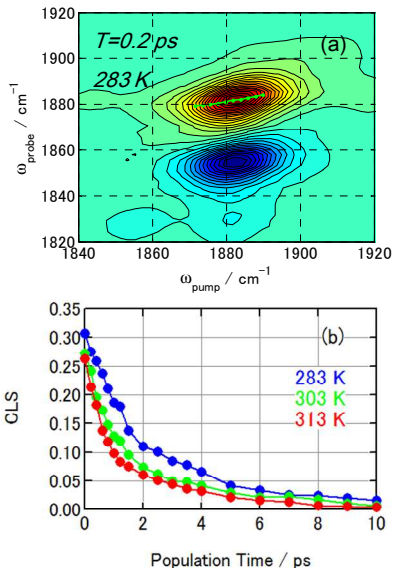

Fig. 1 (a) 2D IR spectrum at 283 K. (b) CLS decay curves at different temperatures.

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Ultrafast Vis-Pump/IR-Probe and Transient 2D-IR Investigation of the Excited State Dynamics of *trans*-β-apo-8'-carotenal

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We have studied the excited state relaxation dynamics of the carbonyl carotenoid *trans*-8'-apo-β-carotenal by means of transient infrared spectroscopy (T1D-IR), transient 2D infrared spectroscopy (T2D-IR) and quantum chemical calculations. Measurements performed in different solvents showed a polarity induced lifetime shortening, typical of carotenoids containing a carbonyl group, and ascribed to the presence of an excited state with intramolecular charge transfer character (ICT). Important information is obtained by analysing diagnostic modes in the T1D-IR spectrum, in particular the C=C symmetric mode, absorbing at *ca* 1550 cm^{-1} in the ground state, which upshifs by more than 100 cm^{-1} in the excited state. Transient spectra in cyclohexane show a single band at *ca* 1750 cm^{-1} due to the C=C mode in the excited state, while measures performed in chloroform evidence the presence of a double peaked band, with maxima at 1685 and 1715 cm^{-1}, showing a different rising time. The doublet is clearly visible in the T2D-IR maps. Based on global analysis of the time resolved data and CASPT2/CASSCF (or TD-DFT) quantum chemical calculations of energies, vibrational frequencies and possible decay paths, we propose a kinetic scheme for the polarity-dependant relaxation dynamics of *trans*-8'-apo-β-carotenal, and investigate the nature of the ICT state. In our scheme the ICT state is the Bu^+ state, which in polar solvents becomes the lowest excited singlet following the stabilization due to conformational changes and solvent relaxation change.

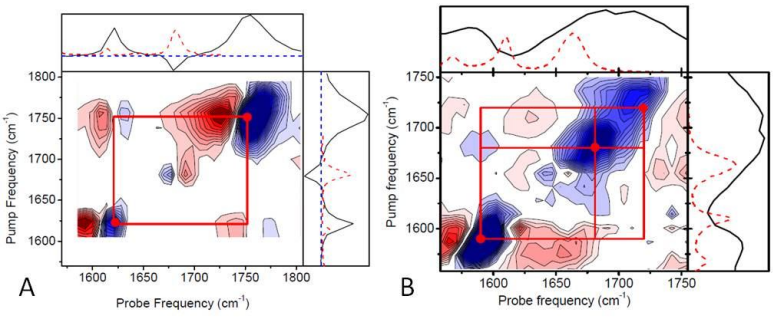

Figure 1: T2D-IR spectra measured A) in cyclohexane and B) in chloroform of *trans*-8'-apo-β-carotenal, using a visible pump at 400 nm, withVis-pump/IR-pump delay of 3 ps and IR-pump/IR-probe delay of 500 fs.

Band merger and intensity bias in 1D and 2D vibrational spectra arising from coupling between different isotopic species

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The isotopic substitution technique is widely used to effectively decouple a particular vibration from the others in the presence of strong intermolecular (or inter-peptide) vibrational interactions, for the purpose of simplification of the interpretation of the spectral profiles. For example, in the case of the OH stretch, the H/D substitution is surely useful for this purpose, because of the very large frequency separation between the OH stretch and the OD stretch. However, in many other cases of isotopic substitution, e.g., in the case of the amide I mode of the peptide groups in proteins upon ^{12}C=O/^{13}C=O substitution, a nearly resonant situation is considered to occur, because the frequency separation is not so large. Then, what kind of spectral features can we expect for those cases?

In the present work, we study the case of the C=O stretching (amide I) mode of three 1:1 isotopic binary liquid mixtures of *N,N*-dimethylformamide (DMF): DMF/DMF-d_1, DMF/DMF-d_6, and DMF/DMF-^{13}C=O [1]. It is shown that band merger and intensity bias (of the bands of different species) are seen in the isotropic Raman spectra, and the opposite intensity bias occurs in the 2D-IR spectra. The vibrational coupling giving rise to these phenomena will be discussed.

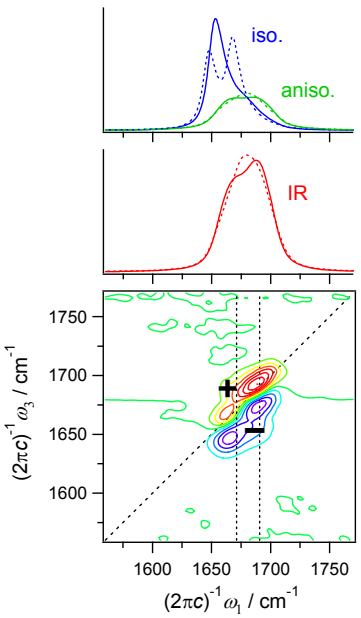

Fig. 1 1D and 2D spectra of the 1:1 DMF/DMF-d_1 binary liquid mixture. The broken curves in the 1D spectra are the spectra synthesized from those of the two neat liquids.

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Real-time wavepacket dynamics through a conical intersection

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Since the conversion of the 11-*cis* retinal chromophore to its all-*trans* form in rhodopsin was identified as the primary photochemical event in vision, experimentalists and theoreticians have tried to unravel the molecular details of this process. Rhodopsin's unique reactivity is generally attributed to a conical intersection between the potential energy surfaces of the ground and excited electronic states and thereby enables the efficient and ultrafast conversion of photon energy into chemical energy. But obtaining direct experimental evidence for the involvement of a conical intersection is challenging: the energy gap between the electronic states of the reacting molecule changes significantly over an ultrashort timescale, calling for observational methods that combine high temporal resolution and a broad spectral observation window. Here we show that ultrafast optical spectroscopy with sub-20-fs time resolution and spectral coverage from the visible to the near-infrared allows us to follow rhodopsin isomerisation in real time. We track coherent wave-packet motion from the photoexcited Franck–Condon region to the photoproduct by monitoring the loss of reactant emission and the subsequent appearance of photoproduct absorption, and find excellent agreement between the experimental observations and molecular dynamics calculations that involve a true electronic states crossing [1]. Taken together, these findings constitute the most compelling evidence to date for the existence and importance of conical intersections in visual photochemistry.

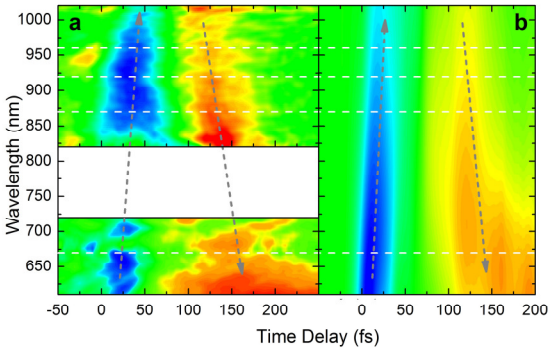

Fig. 1 Experimental (a) and simulated (b) wave-packet dynamics through the rhodopsin conical intersection.

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Time-resolved spectroscopy of J-aggregates with sub-10-fs resolution

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Some kinds of dye molecules dissolved in solution with concentration exceeding a certain level form J-aggregates, nanostructures with sizes intermediate between molecular crystals and isolated molecules. Because the optical properties of J-aggregates have been attracting great interest for future applications to photoelectric cells and nonlinear optical devices, they have been extensively studied both experimentally and theoretically [1, 2]. However, it has yet to be determined how the structures of J-aggregates are correlated with its strongly correlated electronically excited state forming an exciton state because of very weak exciton-phonon coupling in the Frenkel excitons of the J-aggregates. The photophysical properties including temperature dependence of the J-aggregates of 3,3‘-disulfopropyl-5,5’-dichloro-9-ethylthiacarbocyanine (THIATS) in various aqueous solution, which is classified in cyanine dye family, have been studied by stationary absorption and fluorescence spectroscopy together with time-resolved fluorescence measurement. However, time-resolved absorption dynamics, molecular vibrational properties and Raman spectra of THIATS have not yet been studied. It is therefore interesting to apply time-resolved impulsive stimulated Raman scattering measurements to the molecular aggregates.

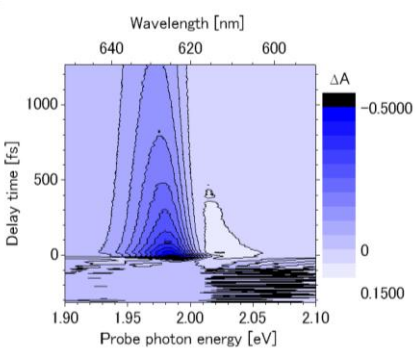

Fig. 1 2D-ΔA spectrum.

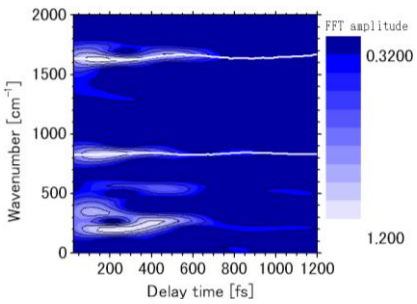

Fig. 2 The spectrogram.

We performed ultrafast pump–probe spectroscopy of J-aggregates of THIATS and detected excited molecular vibrations, using sub-10-fs pulse-laser. The time-resolved two-dimensional difference absorption (ΔA) spectra were observed between -314 and 1267 fs. By performing the spectrogram analysis, there was a modulation of the vibrational frequencies around 1633 cm^{-1} which depend on the delay time. By the analysis of the modulation, energy flow is found to take place from other (824cm^{-1}) modes to the 1633 cm^{-1} mode through the very low frequency mode with the 50 cm^{-1} [3]. Also, by fitting the real-time traces of ΔA with the sum of two exponential functions and a constant term, the average lifetimes of three electronically-excited state were found to be τ_1=52±5 fs and τ_2=540±78 fs. By performing single-exponential fitting around the stationary absorption peak at 1.990 eV, in the negative time range, the electronic dephasing time, T_2^{ele}, is determined to be 18.30 fs.

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Excited state intramolecular proton transfer dynamics of hydroxyanthraquinones in solution by impulsive excitation of vibrations

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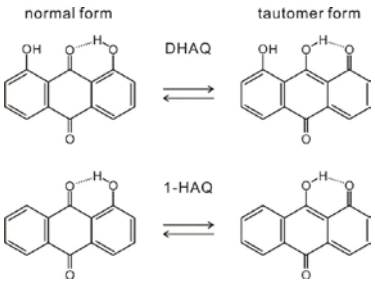
Proton transfer reaction is one of the most fundamental processes in chemistry and biology. Excited state intramolecular proton transfer (ESIPT) has been studied as a model system of the proton transfer, since it can be conveniently initiated by light. We report ESIPT reaction dynamics of 1-hydroxy-anthraquione (1-HAQ)[1] and 1,8-dihydroxyanthraquinone (DHAQ) by highly time-resolved fluorescence (TRF). Normal emission of 1-HAQ is nearly absent, whereas DHAQ shows both normal and tautomer emissions. Wave packet motions of both reactant and product are observed, which allowed detailed description of the ESIPT dynamics for these molecules.



ESIPT time of 1-HAQ is determined to be 45±10 fs directly from the TRF decay of the reactant and rise of the product, whereas ESIPT time of DHAQ is faster occurring in 20 fs. The TRF of 1-HAQ shown in Fig. 1 exhibits two peaks at 217 and 394 cm^{-1}. The TRF of DHAQ gives two peaks at 217 and 360 cm^{-1} from the normal form (reactant) and three peaks at 210, 315, and 442 cm^{-1} from the tautomer form (product). Theoretical analyses show that the vibrational mode excited impulsively by the ESIPT involves symmetric displacements of the quinone oxygens (ν_{11}) predominantly. We suggest that the ν_{11} mode play a significant role for the ESIPT reaction and the ESIPT of both molecules proceed barrierlessly with the assistance of the ν_{11} skeletal vibration, which in turn excites the low frequency vibrations impulsively.

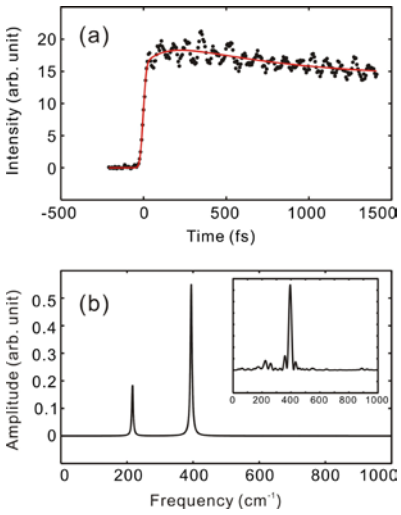


Figure 1. TRF of 1-HAQ tautomer and its Oscillation spectrum by LPSVD and FFT (inset).

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Following excited state evolution with impulsive vibrational spectroscopy

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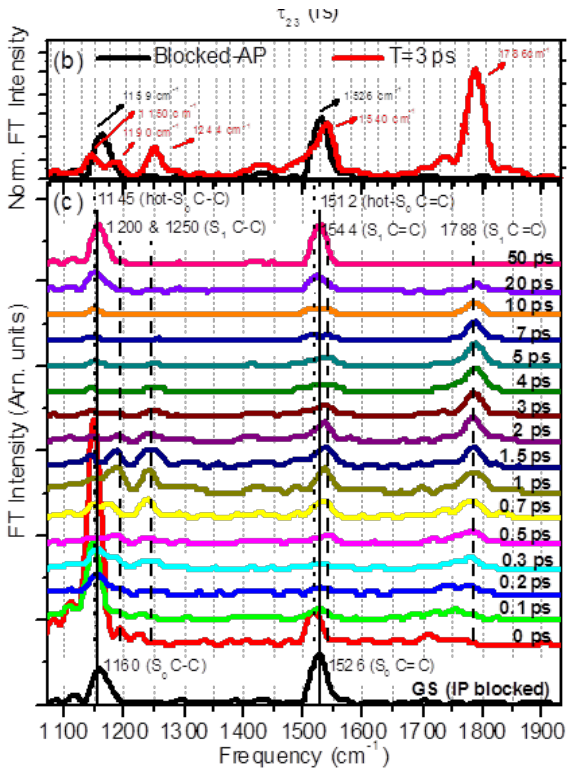

Pump – Impulsive Vibrational Spectroscopy (Pump-IVS) [i] is used to record excited state vibrational dynamics following photoexcitation of beta carotene with. The spectra obtained, ranging in frequency from 100 - 3000 cm^{-1}, cover the course of S_2-S_1 internal conversion, followed by cooling and decay to the ground electronic state. Processed, data, obtained by background subtraction and Fourier analysis are presented in the figure on the left.

Following excitation a ~2 ps buildup of S1 signatures at 1200, 1250 (C-C), 1544 (C=C) and 1790 (C=C) cm^{-1} is apparent. At later delays, following spectral shifting assigned to vibrational cooling, bands indigenous to S_1 (1200, 1250 and 1800) decay exponentially with a ~10 ps timescale. These results demonstrate the potential of pump-IVS to cover photochemical dynamics, including fingerprint frequencies which directly reflect changes of bonding and structure in the nascent sample. In the talk we discuss exclusive strengths of this method and compare it with previously demonstrated capabilities of the related degenerate four wave mixing method[ii], and with the frequency read-out Femtosecond Stimulated Raman Scattering (FSRS)[iii], highlighting the complementary nature of these techniques, and the benefits of using them in concert.

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Water migration dynamics studied by picosecond time-resolved IR spectroscopy

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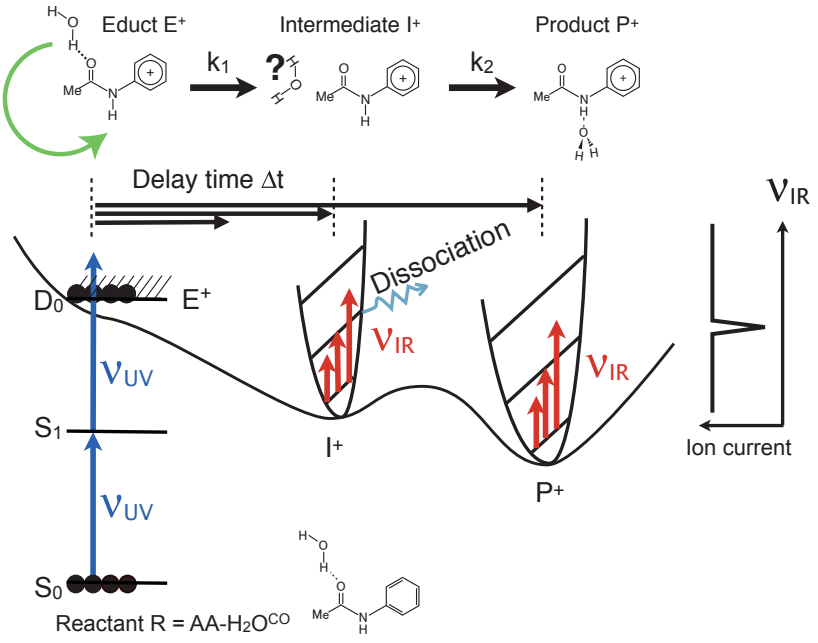
Motion of a single water ligand around the peptide linkage in *trans*-acetanilide (AA) was probed in real time by time-resolved infrared (IR) spectroscopy[1-5] of the isolated AA^+-H_2O cluster cation.[6] In the neutral AA-H_2O dimer, the H_2O ligand is hydrogen-bonded to the CO site of the peptide bond. Triggered by photoionization, the H_2O ligand is released from this binding site and eventually trapped after a migration time of 5 picoseconds at the NH site of the same peptide bond. Time-resolved IR spectra reveal that this water migration is not a simple elementary process but involves an intermediate state, in which H_2O is binding neither to the CO nor the NH site.



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Study on photoisomerization of PYP chromophore by picosecond time-resolved pump-probe spectroscopy in the gas phase

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Coumaric acid and its derivatives are known as model chromophores of the *trans* → *cis* photoisomerization of PYP (Photoacitive Yellow Protein). We recently carried out pump-probe measurements for the S_1 state of methyl-4-hydroxycinnamate (OM_pCA) and its 1:1 hydrogen-bonded complex with water (OM_pCA-H_2O) in the gas phase (Fig. 1) [1]. We found that the S_1 lifetime of bare OM_pCA is 9 ps, while it becomes 930 ps in the complex (Fig. 2). Thus, the H-bonding to the phenolic OH group at *para*-position greatly decelerates the nonradiative process, that is *trans* → *cis* isomerization, of the S_1 state. In addition, we found the lifetime of the OM_pCA-H_2O complex sharply becomes shorter within 500 cm^{-1} above the S_1 origin.

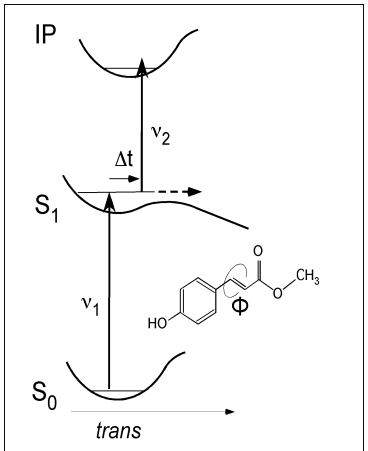

Fig. 1 *Trans* ― *Cis* photoisomerization of OMpCA

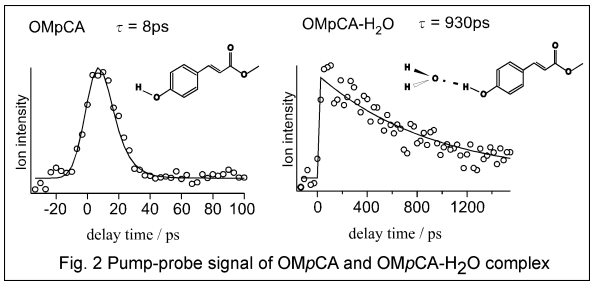

Fig. 2 Pump-probe signal of OM*p*CA and OM*p*CA-H_2O complex

To know more detail about the mechanism of the nonradiative process of OM_pCA and effect of H-bonding, we performed potential energy calculation by SAC-CI method along the isomerization coordinate. We found that the $S_1(\pi\pi^*)$ potential energy smoothly decreases along the isomerization coordinate (ϕ) for bare OM_pCA, while it exhibits ~200 cm^{-1} barrier in OM_pCA-H_2O, which is in good agreement with the experimental observation. In addition we measured the S_1 lifetime of OM_pCA-NH_3 to study the effect of H-bonding strength, and found the lifetime increase as large as 6 ns at the S_1 origin.

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Effects of Hydrogen Bonding on Internal Conversion of GFP-like Chromophores

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To rationalize the quenching of the fluorescence and the $Z \rightarrow E$ photoisomerization of the green fluorescent protein (GFP) chromophore, the femtosecond time-resolved fluorescence and transient infrared (TRIR) spectra of *p*-ABDI, *m*-ABDI, and others in CD_3CN, CH_3OH, and CD_3OD are determined. For *m*-ABDI in CD_3CN, fluorescence decay lifetime is ~7.9 ns and IR absorption lines near 1513, 1531, 1557, and 1613 cm^{-1} of *m*-ABDI in its electronically excited state were observed with a decay time >5 ns. For solutions in CH_3OH, the fluorescence decay is double exponential with time constants ~16 and 62 ps. In addition to IR absorption lines of *m*-ABDI in its electronically excited state with decay time ~16 ps, new features near 1513, 1532,1554, and 1592 cm^{-1} were observed to have a rise time of ~19 ps and a decay constant of ~58 ps, indicating formation of an intermediate. We conclude that the torsion of the exocyclic C=C bond (the τ torsion) is responsible for the nonradiative decay of electronically excited *m*-ABDI in CD_3CN. However, in CH_3OH and CD_3OD, the solute-solvent hydrogen bonding (SSHB) interactions diminish significantly the barrier of the τ torsion and induce a new pathway that competes successfully with the τ torsion, consistent with the efficient fluorescence quenching and the diminished yield for $Z \rightarrow E$ photoisomerization. The new pathway is likely associated with excited-state proton transfer (ESPT) from the solvent to *m*-ABDI, particularly the carbonyl group, and generates an intermediate (ESPT*) that is weakly fluorescent.
Results of other GFP chromophores will also be presented.

References:

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Excited-state multiple proton transfer in solvated 7-azaindole clusters

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Picoseconds pump and probe experiment has been applied to study the excited state dynamics of 7-azaindole-water 1:2 and 1:3 clusters [7AI$(H_2O)_{2,3}$] in the gas phase. The vibration-mode selective Excited-State-Triple-Proton Transfer (ESTPT) in 7AI$(H_2O)_2$ proposed from the frequency-resolved study has been confirmed by picosecond decays [1,2]. The decay times for the vibronic states involving the ESTPT promoting mode $\sigma(1)$ (850~1000 ps) are much shorter than those for the other vibronic states (2100~4600 ps). In the (1+1) Resonance-Enhanced Multiphoton Ionization (REMPI) spectrum of 7AI$(H_2O)_3$ measured by nanosecond laser pulses, the vibronic bands with an energy higher than 200 cm^{-1} above the origin of the S_1 state become very weak. In contrast, the vibronic bands in the same region emerge in the (1+1') REMPI spectrum of 7AI$(H_2O)_3$ with picoseconds pulses. The decay times drastically decrease with increasing the vibrational energy above 200 cm^{-1}. Ab-initio calculations show that a second stable "cyclic-nonplanar isomer" exists in addition to "bridged-planar isomer" (Fig. 1), and that an isomerization from bridged-planar isomer to cyclic-nonplanar isomer is responsible for the short lifetimes of the vibronic states of 7AI$(H_2O)_3$. The IR-dip spectra in the S_1 state indicated that cyclic-nonplanar isomer was produced after the excitation of the normal form. It has been found that a structural fluctuation occurs between bridged-planar isomer and cyclic-nonplanar isomer when the $S_1(0\text{-}0)$ transition was excited.

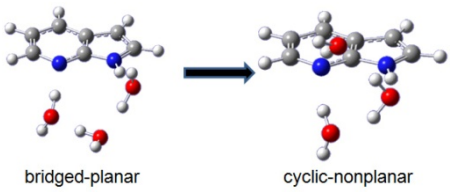

Fig.1 Isomerization of 7AI$(H_2O)_3$

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Oral Presentation
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Studies of Organic Monolayers at Water interfaces

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Adsorption of organic monolayers at a water interface drastically modifies the interfacial properties. It is a subject of great interest in connection with many applications. How ions in water affect the interfacial structure and properties, in particular, has attracted much attention in recent years. An adsorbed organic monolayer at an interface can induce a higher concentration of positive or negative ions and set up a surface field near the interface, causing water molecules near the interface to reorient.[1] On the other hand, ions at the interface can affect the equilibrium structure of the adsorbed monolayer. For example, at a given surface pressure, the surface density of a charged surfactant monolayer on water must depend on the pH or salt concentration in water because the surface ions change the Coulomb interactions between neighboring organic molecules in the monolayer. [2]

Sum-frequency vibrational spectroscopy (SFVS) is an effective tool to study organic monolayer/water interfacial systems. We use phase-sensitive SFVS to probe the effects of solvated ions on the structure of an amphiphilic monolayer/water interface at a fixed surface density. While the surface ions have no effect on the molecular configuration, they can protonate/deprotonate the hydroxyl terminals of the organic molecules, charging the interface and reorient the interfacial water molecules. In probing the interfacial water structure with SFVS, care is taken to make sure that the bulk contribution of water is negligible. We also use SFVS to investigate the effect of solvated ions on the structures of hydrophobic organic monolayer/water interfacial systems. Significant interactions between hydrophobic chains and hydroxyl ions are revealed. Studies of interfacial dynamics are in progress.

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Vibrational and reorientational dynamics of interfacial water

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At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water. Owing to its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has received much attention.

We investigate the vibrational and structural dynamics of interfacial water using ultrafast one- and two-dimensional surface-specific sum-frequency generation (SFG) vibrational spectroscopy. In these techniques we excite molecular vibrations at the interface with an intense femtosecond mid-infrared pulse, and we probe the effect of this excitation on the intensity and spectrum of the sum-frequency light that is generated with a delayed mid-infrared and visible probe pulse pair. For the water-air interface, we find that the interface is both structurally heterogeneous and highly dynamical [1]. We determine the timescale on which the heterogeneity decays, reveal the presence of surprisingly rapid inter- and intramolecular energy transfer processes, and quantify the reorientational dynamics of interfacial water molecules [2]. Moreover, we find that there are different, distinct contributions to the relaxation of vibrationally excited states at the interface [3].

Finally, we show, using isotopic dilution experiments in conjunction with path-integral molecular dynamics simulations, that the inherent symmetry breaking of the interface creates a macroscopic nuclear quantum effect not present in bulk water [4].

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2D Heterodyne-Detected VSFG Spectroscopy of Water at Aqueous Interfaces

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Understanding vibrational dynamics of water at interfaces is of great importance in many fundamental and applied sciences including physics, chemistry, biophysics etc. However, the dynamics of interfacial water is poorly understood compared with the wealth of knowledge about bulk water dynamics because of the lack of a suitable time-resolved spectroscopic method for interfaces. Recently, as an extension of our steady-state heterodyne-detected vibrational sum frequency generation (HD-VSFG) technique [1, 2], we have developed time-resolved heterodyne-detected VSFG (TR-HD-VSFG) [3] and 2D-HD-VSFG [4] spectroscopies to investigate interfacial water dynamics. TR-HD-VSFG provides the imaginary part of a pump-induced change in $\chi^{(2)}$ ($\Delta \mathrm{Im}\chi^{(2)}$, $\chi^{(2)}$: 2^{nd} order nonlinear susceptibility), which can be readily compared with bulk transient infrared spectra that correspond to $\Delta \mathrm{Im}\chi^{(1)}$ ($\chi^{(1)}$; linear susceptibility). Likewise, 2D-HD-VSFG provides an interface-specific 2D vibrational spectrum which is the direct counterpart of 2D-IR spectrum of bulk water. Using these techniques combined with isotopic dilution technique, we have explored the water dynamics at charged interface. In this presentation, we report the development of TR- and 2D- HD-VSFG spectroscopies and our most recent results about the vibrational dynamics at aqueous interfaces.

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Vibrational dynamics of adsorbates on metal surfaces studied by time-resolved sum-frequency generation

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Femtosecond laser excitations on a metal surface can induce its electron temperature rise up to several thousand Kelvin due to a low heat capacity of electrons. Subsequently, energy transfer to adsorbate vibration occurs via non-adiabatic couplings leading to various surface reactions. The hot-electron mediated process occurs within a sub-picosecond time scale, and a surface sensitive vibrational spectroscopy with high time resolution is necessary to reveal the mechanism.

In this talk, we report on our recent achievement in combining a phase-sensitive detection with femtosecond IR-visible sum-frequency generation (SFG) spectroscopy under an ultrahigh vacuum conditions [1,2]. Photo-induced desorption of carbon monoxide from Pt(111) and Cu(100) upon excitation with 400 nm, 150 fs pulse is studied by monitoring transient SFG signals of the C-O stretching mode. The novel technique enables us to reconstruct the vibrational polarization in the time domain. The time-resolved signals show transient frequency shifts and amplitude decrease in a sub-picosecond time range due to the excitation of CO-metal frustrated modes coupled with substrate hot-electrons (Fig. 1). By analyzing the transient modulation of the vibrational polarization, we succeeded in gaining insight into the precursor states of the photo-induced desorption.

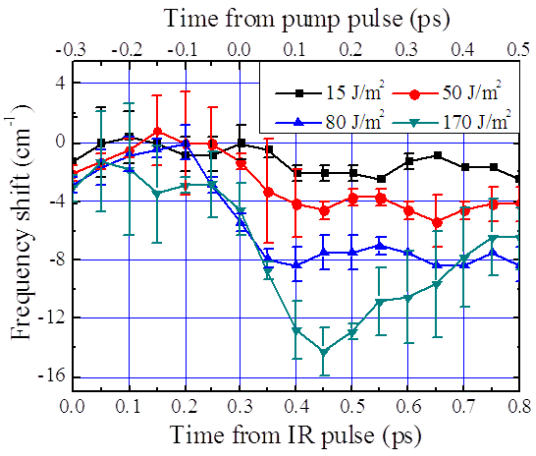

Fig. 1: Transient frequency shift of C-O mode on Cu(100) upon excitation with 400 nm pump.

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Heme cyanide photodissociation in myoglobin and horseradish peroxidase

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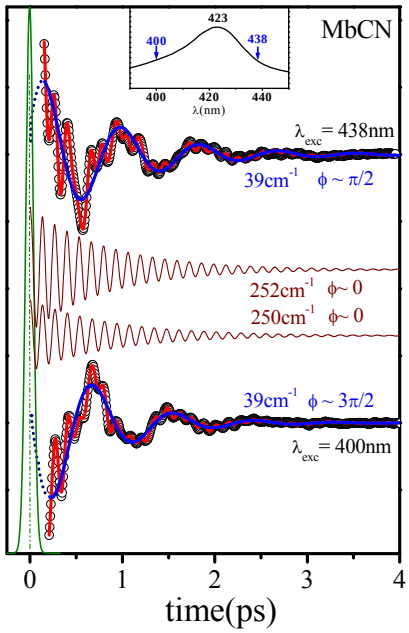
The photodissociation of cyanide from ferric myoglobin (MbCN) and horseradish peroxidase (HRPCN) has implications for the interpretation of ultrafast IR [1] and optical [2] studies that had previously suggested the heme Fe-CN bond was photostable. The photolysis of ferric MbCN takes place with a quantum yield of ~75% and the resonance Raman spectrum of the photoproduct is identical to that of ferric Mb (metMb). The data are quantitatively analyzed using a simple model where cyanide is photodissociated and, although geminate rebinding with a rate $k_{BA} \approx (3.6\ ps)^{-1}$ is the dominant process, some CN^- exits from the distal heme pocket and is replaced by water. We find that the CN^- escape rate from the ferric myoglobin pocket to the solution at 293 K is $k_{out} \approx 1–2 \times 10^7\ s^{-1}$. This value is very similar to, but slightly larger than, the histidine gated escape rate [3] of CO from Mb ($1.1\times10^7\ s^{-1}$) under the same conditions. The analysis leads to an escape probability $k_{out}/(k_{out}+k_{BA}) \sim 10^{-4}$, which is unobservable in most time domain kinetic measurements. However, the photolysis is surprisingly easy to detect in Mb using power dependent cw resonance Raman measurements. This is due to the slow CN^- bimolecular association rate (170 $M^{-1}s^{-1}$), which involves water exchange at the ferric heme. In contrast, ferric HRP does not have a heme bound water and its CN^- bimolecular association rate is larger by $\sim10^3$. These results are consistent with the $\pm\pi/2$ phase of the strong heme doming mode of MbCN that is observed at 39 cm^{-1} in the coherent response following excitation on the red and blue sides of the Soret band (see figure). This phase behavior is indicative of a strong momentum impulse at t=0 associated with photolysis.



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Allosteric dynamics of hemoglobin revealed by time-resolved resonance Raman spectroscopy

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Proteins are endowed with both stiff and flexible properties; hence their dynamics are closely associated with structure and function. Because allosteric proteins in general propagate conformational changes over considerable distances, how these conformational changes are generated and transmitted is of major interest for understanding the regulatory, kinetic, and recognition properties of proteins. A variety of experimental evidences suggests that rapid and long-range propagation of conformational changes through the core of protein plays a vital role in allosteric communication. Time-resolved resonance Raman (RR) spectroscopy provides information on the dynamics of the tertiary and quaternary structures of hemoglobin with the combination of ligand photolysis techniques. In this study, we investigated protein dynamics of recombinant human hemoglobin (rHb) and its isolated chains upon photolysis of carbon monoxide.

In the time-resolved RR spectra, we observed frequency shifts of the iron-histidine stretching [ν(Fe-His)] and γ_7 bands, and an intensity change of the ν_8 band for rHb, showing that a primary metastable form was present in the initial tens of nanoseconds following the photolysis. Similar spectral changes were reported for both the isolated α- and β-chains of rHb. Common spectral changes between the isolated chains and rHb indicated that structural changes reflected by the spectral changes were characteristic of the hemoglobin subunits. The heme modes suggested that the primary metastable form had a more disordered orientation of propionates and a less strained environment than the deoxy form. In spite of the fact that the isolated β-chain formed a tetramer in a similar fashion to rHb, the spectral changes were much slower than those of rHb. The present study shows that intersubunit interactions affected the rates of the structural changes of the heme pocket. Characteristics of the higher-order structure dynamics of hemoglobin are discussed.

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Proteins in Action: Time Resolved Infra-red Study of a Photoactive Flavoprotein from Femtoseconds to Milliseconds

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Protein function is often inferred from protein structure. However, function also involves structural evolution i.e. protein dynamics. The most successful protein dynamics measurements have been in photobiology. However, most such measurements focus on the fs – ns time range. In many proteins functionally important structure changes occur on a much longer time scale. A case in point is the photoactive flavoprotein AppA, a light activated antirepressor. Optical excitation of the flavin gives rise to rapid local changes, which ultimately cause large scale structural change remote from the flavin, leading to release of the repressor PpsR. Fast local changes have been probed by ultrafast visible and IR spectroscopy.[1] The final state has been probed by IR difference spectroscopy. The missing ns - ms time scale is where the protein structure evolution actually occurs.

In this work we present measurement of transient IR difference spectra of AppA with <10 μOD sensitivity in the temporal range 100 fs to 1 ms.[2] We observe the bleach and recovery of the flavin. The ultrafast perturbation to the protein matrix of AppA is time resolved and assigned. Critically, subsequent development of the final state as measured in IR difference spectroscopy is time resolved. We find that large scale change in protein structure is fast, occurring in microseconds. The pathway of structure change in AppA is probed by mutagenesis.

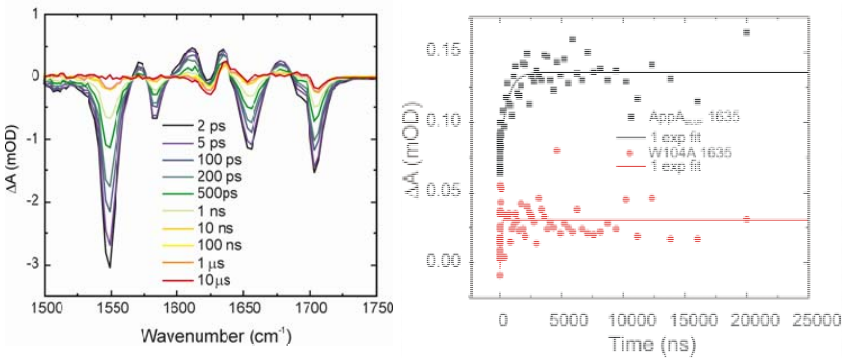

Figure. (a) Time resolved IR of AppA from fs to ms. (b) shows the effect of a point mutation.

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Proton transfer and photoswitching in Fluorescent Proteins

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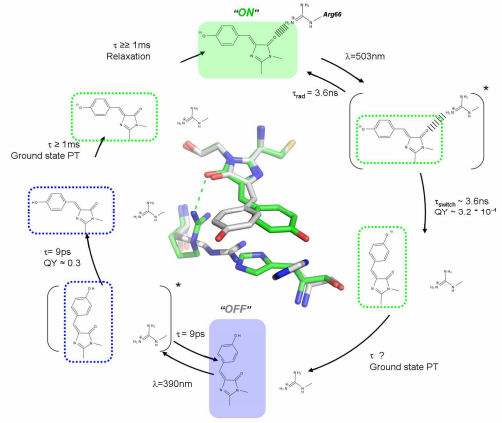
Proton transfer reactions are key in developing spectroscopic contrast in Fluorescent proteins. While the original *a. victoria* GFP is unique in being the only protein which exhibits Excited State Proton Transfer (ESPT) [1], there also exist other fluorescent proteins which undergo photoswitching reactions and are commonly used in applications such as super-resolution microscopy. The reversible photoswitching between the 'On' and 'Off' states of the fluorescent protein Dronpa are known to involve photoisomerisation, protein side-chain rearrangements, as well as proton transfer events. These proton transfers have been proposed, by analogy to *a. victoria* GFP, to involve ESPT. We report on time resolved infrared spectroscopy which shows that light-induced deprotonation of the chromophore phenolic oxygen in the 'Off' state is a thermal ground-state process, which follows ultrafast (9 ps) trans–cis photoisomerization, and so does not involve excited-state proton transfer [2]. Steady-state infrared difference measurements excludes protonation of the imidazolinone nitrogen in both the 'On' and 'Off' states. Ultrafast pump–probe infrared measurements of the 'On' state reveals a weakening of the hydrogen bonding between Arg66 and the chromophore C=O in the singlet excited state of the cis anionic structure, which could be central to initiating structural rearrangement of Arg66 and His193 coinciding with the low quantum yield cis–trans photoisomerization



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Femtosecond stimulated Raman scattering of S_1 *trans*- and *cis* stilbene

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Stilbene is a prototypical molecule showing photoisomerization. We recently carried out fs stimulated Raman scattering and transient absorption measurements following UV excitation into the S_1 state. Isotopomers D0, D2, D10, D12, ^{13}C2 were examined with 50 fs time-resolution in n-hexane. Many S_1 Raman lines are detected for the first time [1]. We do not see transient shifts of the ~220 cm^{-1} mode of S_1 *cis*-stilbene [2]. Short-lived absorption in the UV [3] is characterized kinetically and thus assigned to the perpendicular conformation.

Vibrational spectra of *trans*-stilbene were calculated at MP2/cc-pVTZ (for S_0) and XMCQDPT2/cc-pVTZ (for S_1) levels of theory. The transition state is C2-symmetric, with central dihedral angle ~120° and phenyl rings in-plane with the central ethylenic bond. The calculated 298 K Gibbs energy correction for the transition state is ca. 1 kJ/mol higher in D2-stilbene compared to D0. In the limit of transition-state theory this translates into ca. 1.5-fold difference in reaction rate. The same is found for the D10-D12 pair.

trans-stilbene was also excited with increasing photon energy. After excitation near the origin at 326 nm, the ethylenic C=C stretching line (~1570 cm^{-1}) broadens by ~2 cm^{-1} due to energy exchange with the solvent. Excitation at 267 nm is followed by 20 cm^{-1} narrowing instead. The effect of laser-induced cooling [4] is thus confirmed, but the magnitude of ΔT is still undetermined.

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Vibrational Relaxation of Guanosine Following Ultraviolet Photoexcitation

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Our group has been developing femtosecond stimulated Raman spectroscopy (FSRS) as a probe of ultrafast photochemical dynamics as well as the foundation of a new generation of two-dimensional Raman spectroscopies. This talk will focus on our recent advances using FSRS to probe the ultrafast relaxation of DNA monomers after ultraviolet (UV) photoexcitation.

For these experiments, a sample of Guanosine 5'-monophosphate (GMP) was excited with a 100-fs 266-nm pulse and the time evolution of the resultant species was measured using FSRS with a 343-nm picosecond Raman pulse (see Figure 1). The observed peaks at 1173, 1260 and 1573 cm^{-1} can be assigned to the vibrationally hot GMP ground-state that is formed in < 1 ps following ultrafast internal conversion from the excited state. However, the peak at 1500 cm^{-1} exhibits distinctive kinetics that may be attributed to the excited state species. Our detailed temperature dependence and anharmonic vibrational calculations aim to clarify the assignment of all the observed bands and the causes of their spectral shifts over the first 5 ps. In particular, an outstanding question remains: Why is the relative intensity of the Raman peaks so different between the ground-state and transient species?

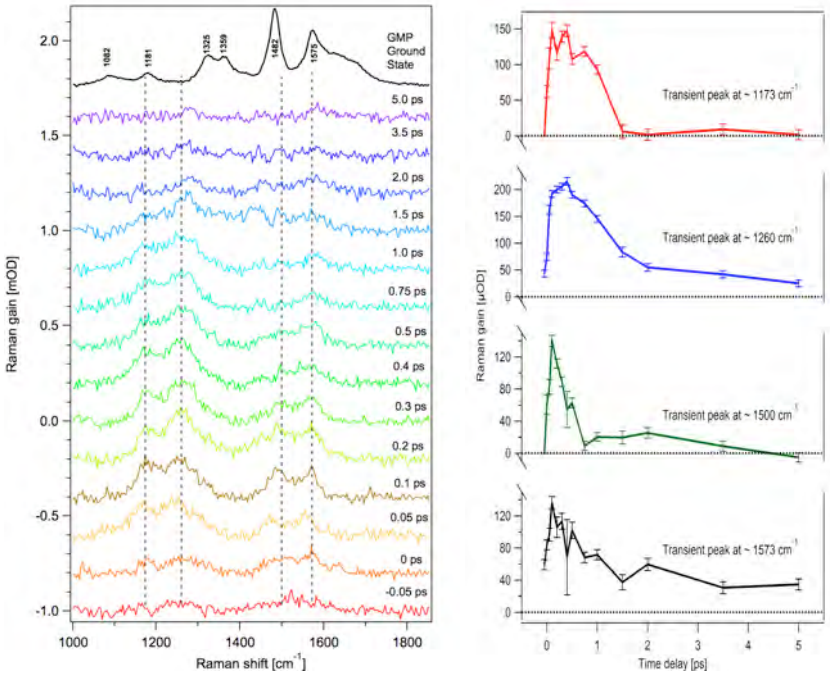

Figure 1. (left) Ground-state and transient FSRS spectra of GMP at various times following photoexcitation with a 266-nm pulse. (right) Kinetics of the observed transient FSRS peaks.

Sub-ps photoinduced dynamics in Heme-proteins studied by Femtosecond Stimulated Resonance Raman Scattering

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Time Resolved Resonance Raman (TR^3) is a powerful technique to study protein dynamics, whose time resolution has been improved over the years from microseconds to a few picoseconds. If a sharp spectral resolution ($<15cm^{-1}$) is to be maintained, however, no further improvement of the time resolution (<1ps) is obtainable due to Heisenberg's uncertainty principle. Moreover, the signals can be weak due to the low spontaneous Raman cross section.
Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful method for studying chemical and biochemical reaction dynamics driven by short laser pulses, in which the simultaneous presence of two electric fields stimulates the Raman transitions. Using dispersed detection, the spectral resolution is fundamentally limited by only the evolution and dephasing of an induced vibrational coherence, whereas the time resolution in principle only depends on the duration of the laser pulses that initiate the photochemical reaction (actinic pump) and the vibrational coherence itself (Raman probe). This "disentanglement" of time and energy resolution (approaching 30fs and $15cm^{-1}$, respectively) reveals a more precise picture of the vibrational dynamics than traditional transient vibrational spectroscopy techniques.
The observation of primary events and ultrafast dynamics of photoactive proteins is so a straightforward application for the FSRS. Moreover we recently combined the principles of FSRS and TR^3, developing a Femtosecond Stimulated Resonance Raman (FSRRS) setup with a broadly tunable narrow-bandwidth Raman pump in the range 350-750 nm [1,2], to be resonant with several molecular transition and especially to cover the region of heme-proteins absorption bands.
Here we want to report the observation of photoinduced bond-breaking dynamics in heme-proteins: the dissociation of a small ligand from the heme in prototypical Myoglobin, and the bond breaking between the heme and the protein backbone in Neuroglobin. The ability to tune the Raman pump on the resonance of the final photoproduct as well as on the absorption of the transient states developing in the first 500 fs allows us to unveil all the details of the nuclear dynamics accompanying bond rupture.
In particular it seems we observed for the first time the bond breaking of the axial histidine which, even in absence of an external molecule, occupies the ligand site in six coordinated deoxy-Ngb, so inducing by light the physiological step enabling ligation.

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Difference of the carotenoid S* state between light harvesting complex and solution revealed by femtosecond stimulated Raman spectroscopy

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In light harvesting (LH) complexes of photosynthetic purple bacteria, light energy is absorbed by carotenoid (Car) and transferred to bacteriochlorophyll (BChl). The S_2 and S_1 excited states in carotenoids are important in the LH function. Another dark excited state (S*) has been identified in carotenoid, but some controversy has been remained in S*. Figure 1 shows species associated Raman spectra of carotenoid in LH1 and cyclohexane solution obtained by resonant femtosecond stimulated Raman spectroscopy (FSRS). The Raman signal of S_1 is identical in LH1 and solution. The transient high frequency shift of the C=C stretching mode (ν_1) is observed and explained in terms of vibrational relaxation of hot S_1. However, the signal of S^*_{LH1} is different from that of S^*_{sol}. Similarity between S^*_{LH1} and the triplet state (T_1) is consistent with the previous report that S^*_{LH1} is a precursor of T_1[1]. On the other hand, S^*_{sol} is suggested to be the hot S_0 state.

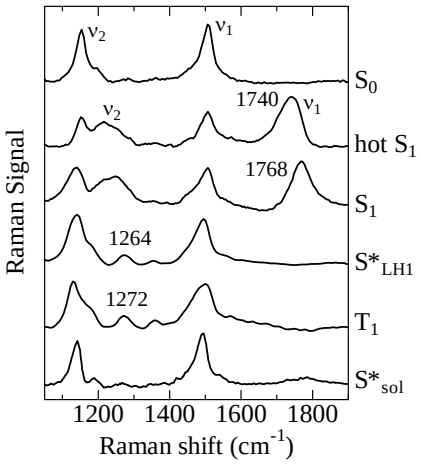

Fig. 1 Species associated Raman spectra.

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Femtosecond near-IR multiplex stimulated Raman gain and loss spectroscopy of β-carotene in 1.0 – 1.6 μm region

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Structure and relaxation dynamics of carotenoids in excited states have attracted much attention in terms of basic physical chemistry as well as of biochemistry. One of the carotenoid molecules, β-carotene, is photoexcited to the S_2 ($1B_u^+$) state with photoexcitation at 480 nm and then decays to the S_1 ($2A_g^-$) state with a time constant of ca. 200 fs [1]. Because the lifetime of the S_2 state is short, neither peak position nor bandwidth of the vibrational bands is well determined for the S_2 state [2,3]. In this study, we try to observe a Raman spectrum of the S_2 state as well as the S_1 state with a femtosecond time-resolved near-IR multiplex stimulated Raman spectrometer.

The sample is photoexcited by the pump pulse (480 nm), and stimulated Raman spectra of the photoexcited species are recorded with the narrowband Raman pump (1188 nm) and broadband probe (1000–1600 nm) pulses. The recorded stimulated Raman gain and loss spectra are shown in Fig. 1. The Raman gain spectrum at 0 ps shows a broad Raman band at 1586 cm^{-1} with a bandwidth of ~100 cm^{-1}. The 1586-cm^{-1} band is observed in the Raman loss spectrum at 0 ps as well, with a similar bandwidth. We assign the 1586-cm^{-1} band to the C=C stretch vibration of the S_2 state. The decay of the S_2 state and rise of the S_1 state are clearly observed from 0 to 0.60 ps.

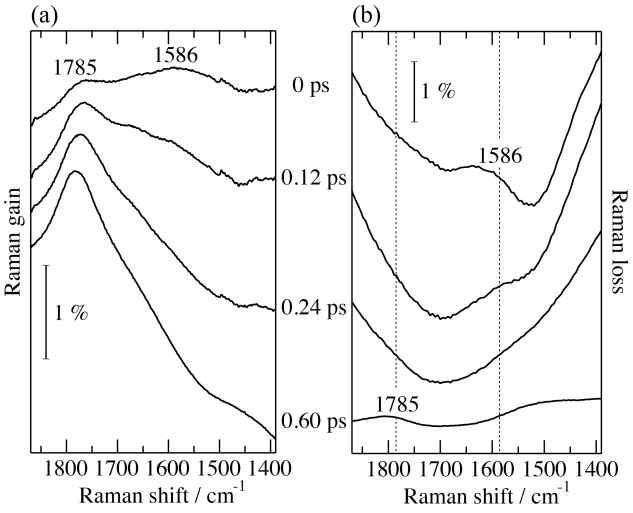

Fig. 1 Time-resolved stimulated Raman gain (a) and loss (b) spectra of β-carotene.

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New insights into the reactivity, ordering, and structure of the low-lying excited triplet states of aromatic compounds as provided by time-resolved near/mid-IR spectroscopy

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After photoexcitation within the singlet manifold and following ultrafast intersystem crossing, low-lying excited triplet states serve as a primary channel through which photochemical and/or photophysical reactions take place. The reactivity and energy-level ordering as well as the molecular structure of low-lying triplet states thus play a determining role in the reactions. However, conventional spectroscopies have been unable to provide direct, experimental insights into those critical properties. In the present study, we have demonstrated the power of nanosecond time-resolved near/mid-IR (TR-NIR/MIR) spectroscopy for unraveling the excited state chemistry of some prototypical aromatic compounds in solution.

We used TR-NIR spectroscopy to establish the relation between the photoreduction activity of acetophenone derivatives and the ordering of their low-lying nπ* and ππ* excited triplet states [1]. In the transient NIR spectra, triplet–triplet transitions from nπ* T_1 and ππ* T_1 states are both observed as broad bands and their relative intensity varies considerably depending on the substituent. The intensity ratio is found to correlate well with the photoreduction activity. We interpret these results in terms of thermal equilibrium between the nπ* and ππ* states. To verify this hypothesis, we examined the temperature effect on the transient bands, from which the enthalpy difference was obtained experimentally, for the first time, to be 2.9 kJ mol^{-1} (≈ 240 cm^{-1}) for methoxyacetophenone.

Furthermore we applied TR-MIR spectroscopy to investigate the molecular structure of *p*-nitroaniline (PNA) in the T_1 state [2]. The MIR spectra of PNA and its isotopomers in the T_1 state are reproduced well by DFT calculations with an explicitly solvated model. Our results indicate that T_1 PNA has a unique partial quinoid structure, which is in stark contrast with a neutral form (the S_0 state) and a charge-transfer zwitterionic form (the S_1 state).

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Electronic and vibrational coherence during the initial charge separation in Photosynthesis

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The very efficient initial charge separation in photosynthetic reaction centers (see the most relevant molecules inFig.1) is treated within the frame of an extended superexchange model with energy distributed charge transfer states P+BL-, which mediate the coupling to the electron acceptor HL (Fig. 2). The coherent mixture of the excited state P* with the CT-states P+BL- is modulated by a low frequency dimer mode. This combination accounts for the oscillatory features of the decay characteristics [1,2]. In addition a non-exponential fall-off of the decay dynamics is predicted in good agreement with experiments. Moreover, we are able to relate the observed strong Stark-effect in the dimer to a partial charge separation within the dimer, which precedes the final charge transfer to the Pheophytin e HL. We also explain observed deuterium effects [2] and the inverted temperature dependence of the process. Finally we discuss the robustness of the model against mutations, the very special structure arrangements of the dimer P and its positioning relative to the monomer which all together make the process so efficient.

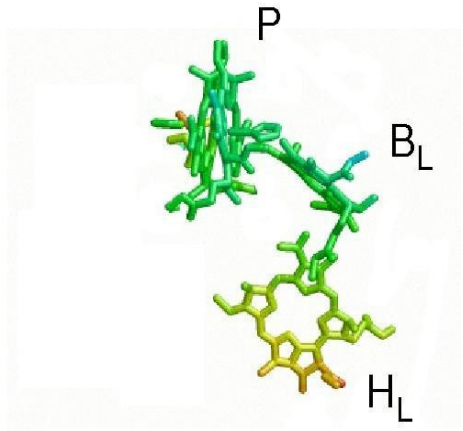

Fig.1: Electron pathway from the dimer P via the monomer BL to the acceptor HL

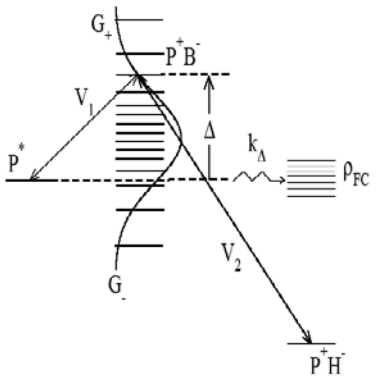

Fig.2: Energies of the excited state dimer P*, the distributed CT-state P+B- and the electron accepting state P+H-

[1] M.H. Vos, F. Rappaport, J.C. Lambry, J. Breton, J.L. Martin, Nature 363 (1993) 320

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Water Potential for Vibrational Spectroscopy

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Recently, we have developed a polarizable water model (POL2VS) for classical molecular dynamics simulations of vibrational spectroscopies, which covers from low-frequency intermolecular modes to high-frequency intramolecular vibrational modes.[1] The model utilizes the ab initio derived geometry-dependent multipole moment surfaces to depict the instantaneous charge density of a water molecule. Multipoles up to quadrupole are included for the permanent multipoles, while those up to dipole are included for the induced multipoles. The polarization of molecules is described by a distributed polarizability model.

At room temperature, the present model is able to reproduce experimental infrared and Raman spectra of intramolecular vibrational modes, except for the blue peak shift due to a limitation of the classical simulation based on a quantum mechanical potential. While the calculated infrared spectrum for low frequency intermolecular modes agreed reasonably well with the experimental signals, we find some discrepancy between the calculated Raman and experimentally observed Raman signal obtained by Heisler, Mazur, and Meech [2] in anisotropic element. In this talk, we examine the cause of this difference. Numerical simulation of the low frequency Raman spectrum for aqueous Alkali Halide solutions will be discussed as an extension of the present research.

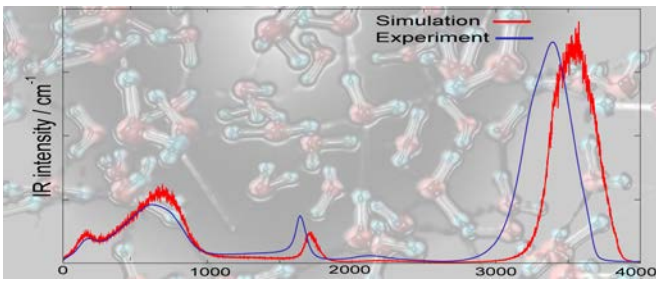

Fig. 1 Calculated IR spectrum of water (Ref[1])

References:

[1] T. Hasegawa, Y. Tanimura, J. Phys. Chem. B **115**, 5545 (2011).
[2] A. Heisler, K. Mazur, S. R. Meech, J. Phys. Chem. B **115**, 1863 (2011).

Anharmonic vibrational structure calculations from the first-principles

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Vibrational structure calculations for large polyatomic molecules remain a challenge because both generating the potential energy surface and solving the vibrational Schrödinger equation becomes exponentially difficult with respect to the size of systems. In this presentation, I will first give a brief summary on our recent development to overcome this problem:

- Optimized coordinates for vibrational structure calculations [1]
- Multiresolution method to construct an accurate potential energy surface [2]
- Vibrational quasi-degenerate perturbation theory [3]

Then, I will show applications of the developed method to hydrogen bonded systems: guanine-water cluster, DNA base pairs [4], etc. Finally, some perspectives toward biological systems are presented.

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[1] K. Yagi, M. Keçeli, and S. Hirata, J. Chem. Phys. **137**, 204118 (2012).
[2] K. Yagi, S. Hirata, and K. Hirao, Theor. Chem. Acc. **118**, 681 (2007).
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Oral Presentation Wednesday

Exciton Delocalization Processes of Various π-Expanded Oligothiophenes

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π-Conjugated organic materials show attractive semiconducting and optical properties combined with solution processability, which makes them highly interesting materials with a great potential for applications in organic electronic devices and molecular electronics. Among these, π-conjugated systems composed of thiophenes have attracted much attention as one of the best candidates to be utilized as components of molecular electronics, mainly because the high polarizability of sulfur atoms in thiophene rings leads to a stabilization of π-conjugated chain and consequently excellent charge transport properties.

Poly- and oligothiophenes intrinsically suffer from strong electron-phonon couplings, which make it difficult to realize the desired properties. To circumvent this drawback, in recent years, a multitude of size- and shape-persistent oligothiophenes have been developed and characterized [1]. However, in spite of these efforts, the excited state dynamics dominated by electron-phonon couplings have not been clearly resolved. In this regard, we have comparatively investigated the size- and shape-dependence of the photophysical properties of linear, star-shaped, and macrocyclic oligothiophenes by using time-resolved spectroscopic techniques at ensemble and single-molecule levels. Based on our experimental results, we have revealed the mechanism of exciton dynamics such as self-trapping, dynamic planarization and excitation energy transfer which allows us to establish valuable structure-property relationships in various oligothiophenes.

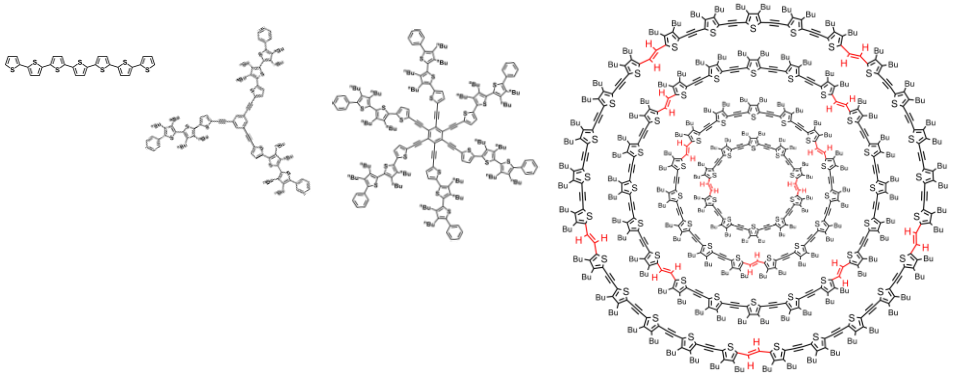

Fig. 1 Linear, star-shaped and macrocyclic oligothiophenes

Reference:

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Vibrational energy transport through molecules

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We have developed two techniques to measure vibrational energy transport through molecules. Both techniques allow us to input vibrational energy at a specific part of a molecule and then probe its arrival at another part. Most studies of vibrational relaxation focus on the movement of vibrational energy from level to level. In our studies, we focus on the movement of vibrational energy through space. In the first technique, that uses 3D IR-Raman spectroscopy, we pump energy into molecular vibrations using short-duration IR pulses and we probe the parent and daughter vibrations using Raman spectroscopy. By tuning the IR pulses while observing the anti-Stokes Raman the transitions, we find IR pulses that produce the most localized initial excitations, and then we watch the energy move through the molecules. As a specific example, in nitromethane we pumped either the nitro groups or the phenyl groups. We found there was no energy transfer from nitro to phenyl and only a little bit of transfer from phenyl to nitro. So nitrobenzene has unidirectional energy transfer. Some other substituted benzenes will also be discussed. In the second technique, a self-assembled monolayer (SAM) is adsorbed on a metal surface that is flash-heated by a laser pulse. Energy flows from the metal layer into the SAM to a point that is probed by sum-frequency generation.

Quantifying transition dipole strengths to identify molecular structures

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We report a method for measuring the transition dipole strengths of vibrational transitions by comparing 1D and 2D IR spectra. Transition dipole strengths carry a tremendous amount of information about molecular structure, especially in systems with monomer repeats like the amide I band of proteins. Structural sensitivity arises because the oscillator strength is non-uniformly distributed in coupled systems. For example, two strongly coupled oscillators will give rise to symmetric and antisymmetric modes (Fig. 1) with unequal oscillator strengths. As such, observing a vibrational mode with a transition dipole strength that is larger than a monomer reveals coupling even if the corresponding frequency shift is too small to observe. However, transition dipole strengths are not always utilized, because to do so with linear absorption one needs to know several factors, such as the concentration which cannot always be determined. We demonstrate our method by identifying alpha-helical structure in a polypeptide by its transition dipole strength, even though it absorbs at nearly the same frequency as a random coil. In other applications, we find that amyloid fibers have vibrational excitons that extend over 5 peptide beta-strands and we show that a disordered peptide adopts a helical structure in membrane bilayers by the strength of its transition dipole. Our method is simple to implement into 2D measurements and we think will become a very useful diagnostic for identifying molecular structures, especially in polypeptides.

References:

[1] Maksim Grechko and Martin T. Zanni, J. Chem. Phys. **137**, 184202 (2012)

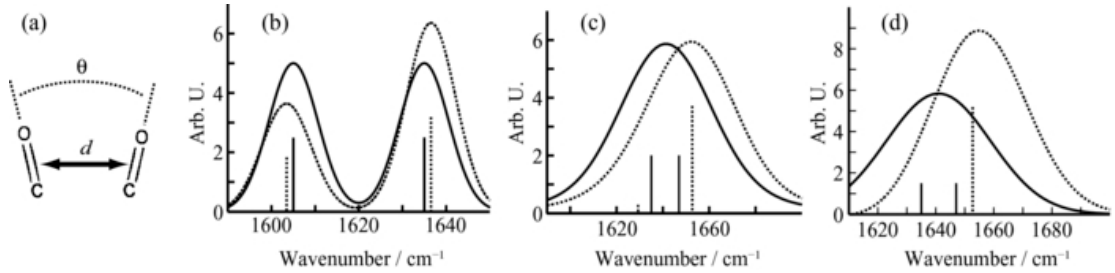

Fig. 1 Illustration of the effects of coupling on transition dipole strengths, frequencies and intensities in 1D and 2D IR spectra. (a) Two carbonyl groups at angle 25° separated by distance *d*. (b) Simulated absorbance spectrum in the uncoupled (solid line) and coupled (dashed line) regime. (c) Simulated absorbance spectrum and (d) diagonal slice of simulated 2D IR spectrum of two near degenerate parallel (θ = 0) oscillators. In (c) and (d) uncoupled and coupled regimes are shown by solid and dashed lines, respectively.

IT10

Monitoring excited-state vibrational dynamics by broadband infrared or Raman probes; A unified picture based on loop diagrams

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Vibrational motions in electronically excited states can be monitored by time and frequency resolved infrared absorption or by off resonant stimulated Raman techniques. Using loop diagrams, which represent forward and backward propagation of the wavefunction we show that both techniques can be described and interpreted using very similar vibrational correlation functions and all our results apply to both techniques with minor modifications. The combined spectral and the temporal resolution of both techniques stem from two interactions with a single device: the infrared probe pulse or a shaped optical pulse, respectively. Nonlinear multidimensional spectroscopy signals depend on several time intervals and there is no conceptual problem in having simultaneous high temporal and spectral resolutions in different independent dimensions, the Fourier uncertainty $\Delta\omega\Delta t > 1$ is never violated.
We have applied a semiclassical approach to simulate the FDIR signal of the RNA nucleobase uracil. Resolving the excited state dynamics of DNA- and RNA- nucleobases has attracted considerably attention in recent years. UV irradiation leads to the population of an electronic state with $\pi\pi^*$ character which is subsequently quenched by internal conversion mediated by conical intersections.

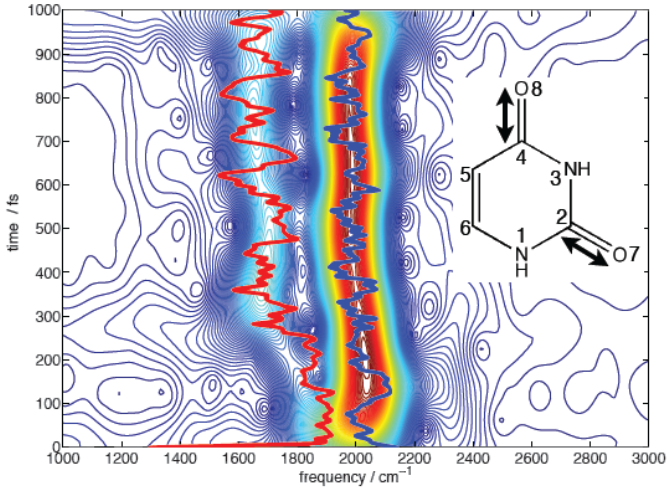

Figure 1: FDIR signal of the RNA base uracil simulated by the semiclassical non-adiabatic on-the-fly molecular dynamics simulations. The $C=O$ marker bands serve as fingerprint to follow the excited state relaxation dynamics.

The time dependent change of $C=O$ marker bands in the FDIR signal is derived from non-adiabatic on-the-fly molecular dynamics simulations. The numerical algorithm developed for the simulation of the time-evolution of specific "fingerprint" modes scales linear with the number of vibrations considered, allowing for simulations of medium sized molecules in the excited states. The predicted signals open the route to unambigously assign the importance of the interconnected reaction pathways in future time resolved measurements.

Structure and dynamics of a drug bound to its allosteric pocket in HIV-1 reverse transcriptase

Daniel Kuroda[1], J. Reddy Challa[1], Thomas Troxler[1], Joseph D. Bauman[2], Disha Patel[2], Kalyan Das[2], Eddy Arnold[2], and Robin M. Hochstrasser[1]

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Infrared spectroscopic studies of the TMC278 complex with the wild-type HIV-1 reverse transcriptase in water[1] have been extended to the clinically relevant mutants: Y181C/K103N and L100I/K103N[2]. FTIR spectra together with 2D IR reveal two transitions in the spectral region of the nitrile stretch vibration at 2215 and 2225 cm^{-1}.[1] Similarities between the IR absorption spectra of the complex in a single crystal (PDB:2ZD1[2]) and in solution demonstrate that each transition corresponds to a nitrile group confined in a different environment[3]. Also, the noticeable spectral broadening observed for the 2225 cm^{-1} transition in the different complex suggests a change in the solvent exposure of the drug.[3] Peak shift dynamics shows a frequency-frequency correlation time of ~1ps, which is assigned to the typical frequency fluctuations produced by water motions.[3] MD simulations show the occurrence of H-bond formation at one nitrile end of the drug in agreement with the blue shift, spectral broadening, and peak shift dynamics observed experimentally for the nitrile stretch located at 2225 cm^{-1}.[3] Also, the simulation results support the proposed change in solvent exposure of the drug. Further, the simulated molecular pictures clearly display the different molecular environments of the drug nitrile groups. Finally, a new high-resolution X-ray crystallography of the wild-type/TMC278 complex (1.5 Å resolution) confirms the presence of water at hydrogen bond distance from one of the nitrile groups.[3]

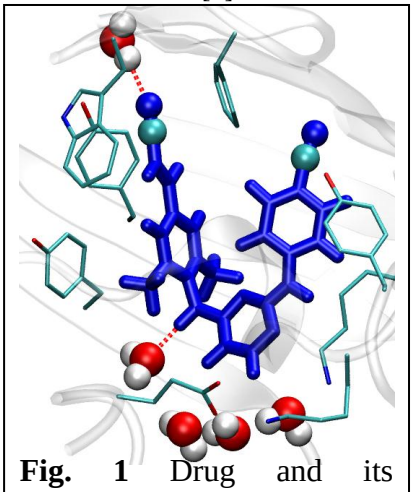

Fig. 1 Drug and its interactions in the pocket of HIV-1 reverse transcriptase.

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Oral Presentation
Thursday

Light-triggered peptides – a new tool for the investigation of ultrafast folding dynamics

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Protein folding is one of the major open problems in Biology. Recently different techniques have been developed in order to gain a better understanding of the folding mechanisms via the investigation of the folding dynamics. In this context vibrational spectroscopy has proven to be an important technique. Interesting results have been obtained from temperature jump (T-jump), experiments giving access to folding processes on the microsecond time scale. Recently we introduced an alternative technique to study even faster processes in folding. We incorporated a light switchable dye into the backbone of a peptide which acts as a structural switch of the peptide with switching speed in the picosecond range. In this talk we will present UV/VIS-pump and IR-probe experiments on such light triggered peptides, and present the hierarchy of photo-physical, photo-chemical and folding processes for hairpin peptides.

The investigations show that light triggering of the molecular switch induces ultrafast structural changes in the directly neighbouring parts of the peptides. We observe IR-transients indicative for the breaking of hydration bonds (within a few picoseconds), for solvent relaxation and cooling within 20 ps and for rearrangements of amino acids adjacent to the switch (200 ps time domain). Within the first nanosecond after light absorption the direct force driven action is finished. It is interesting to note that the structural transients monitored in the IR-spectrum of the amid-1-band are not finished on this time scale. There are pronounced absorption changes pointing to structural dynamics in the microsecond range which finally lead to the stationary spectrum. A careful investigation of temperature dependencies of these long lived transients, and a comparison with T-jump experiments show that the later processes are thermally driven and can be understood as allosteric reactions where the peptide adjusts to the new shape of the molecular switch.

The experiments show that light operated backbone switches are a valuable tool for the investigation of structural dynamics in peptides and proteins. The variety of novel molecular switches for in-vitro and in-vivo applications support the idea that this technique will become a valuable tool for the study of folding reactions and for the initiation of enzymatic reactions in proteins.

Improving signal generation and collection in Femtosecond Stimulated Raman Spectroscopy

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We present recent our recent experimental improvements in signal generation and collection in Femtosecond Stimulated Raman Spectroscopy, with the aim to turn FSRS into a robust, artifact-free and widely applicable form of time-resolved vibrational spectroscopy.

FSRS generally suffers from large spurious background signals that result from dumping and re-pumping of excited molecules by the Raman pump (Rp). In addition, the narrowband FSRS signal is affected by a broadband background originating from the coherent mixing of Rp and probe close to zero time delay, as well as mixing of actinic pump (Pu) and Rp pulses. To address these problems, we have constructed a new wavelength modulator for the Rp based on a custom-made chopper blade and a slit placed in the Fourier plane of a pulse shaper to explicitly record the first derivative of the FSRS signals. This approach resulted in an unprecedented reduction of the non-coherent background that results from population transfer by the Rp. Furthermore, we report that the transient absorption generated by the Pu modulates the overall magnitude of the FSRS signals of the photoactivated sample. As a consequence, the traditional transient FSRS signal is distorted by artifacts, which were observed in the past but left without interpretation. We propose a simple model to calculate the correct transient FSRS signals from the knowledge of transient absorption signal. The model was verified by application to experimental data.

To improve signal gain in FSRS, we designed a novel beam geometry by which simultaneous collinear propagation of the narrowband Rp and spectrally broad probe pulse through an optically long sample leads to exponential amplification of probe pulse at Raman frequencies. By photoexcitation of the sample by a Pu applied from the side and with a tilted wavefront, the sample is efficiently pumped along the focused Rp and probe beams. In this way, the FSRS signal gain is improved by an order of magnitude with respect to traditional noncollinear FSRS experiment, while maintaining sub-ps time resolution.

Revealing excited state nuclear coherence in the photoisomerisation of bacteriorhodopsin by population assisted impulsive Raman

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The 13-cis to all-trans photoisomerisation of the retinal chromophore in bacteriorhodopsin (bR) is a prototypical ultrafast isomerisation process [1]. Within the protein, the reaction is faster, more efficient and more specific than in solution. This variation of chemical reactivity and specificity has spurned decades of spectroscopic investigations to unravel the origin of retinal reactivity in bR. The key remains the reactive entity in the process: the potential energy surface of the reactive excited electronic state that is populated upon absorption of a visible photon. Despite application of numerous ultrafast electronic and vibrational techniques,[2-4] the ultrafast structural evolution of the chromophore after excitation remains effectively unknown. Similarly, the relaxed vibrational structure of the excited state is yet to be determined.

We present recent results on the isomerisation process using a novel approach to study coherent nuclear dynamics associated with ultrafast photochemical processes. Our technique, termed population assisted impulsive Raman spectroscopy (PAIRS), combines high temporal resolution (<20 fs), broadband probing (500-900 nm) and extreme spectroscopic sensitivity ($DT/T \sim 10^{-6}$) with specific electronic population control. Taken together, these properties allow us for the first time to conclusively separate excited from ground state nuclear coherence. Importantly, our approach not only provides vibrational structure, but also the time-dependence of the nuclear dynamics.

The obtained spectra contain a remarkable wealth of information about the potential energy surfaces involved in the photoreaction. Coherent motion in the visible (<750 nm) part of the spectrum strongly resembles the ground state Raman spectrum demonstrating that such an experimental arrangement yields predominantly ground state nuclear wavepacket motion. Except for minor variations in mode intensities, all peaks are reproduced with identical vibrational frequencies within the experimental error. The situation changes dramatically in the near-infrared, a spectral region that is now resonant exclusively with an excited state transition: stimulated emission back to the ground state. The population controlled spectrum now exhibits a completely different intensity pattern with predominantly altered vibrational frequencies. Strikingly, coherent activity is focussed on the low frequency torsional modes (160 cm^{-1}) and hydrogen wagging coordinates (950 cm^{-1}). In contrast, a majority of the initially excited modes (C-C and C=C stretches) predicted by the resonance Raman spectrum is now absent. Our results are in remarkable agreement with a simple model involving backbone torsion and hydrogen wagging as the major coordinates involved in a conical intersection providing efficient passage back to the ground electronic state.

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ime resolved R s ectrosco y of cyclo entane 1 3 diyl iradicals

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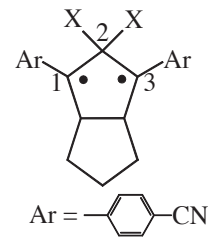
Singlet cyclopentane-1,3-diyl biradicals were first theoretically predicted [1] and were afterward experimentally brought to realization [2]. Subsequent extensive investigation on substitution effects have enabled us to control the spin multiplicities (singlet or triplet) and lifteimes of the biradicals [3]. However, their molecular structure and dynamics were investigated almost entirely by quantum chemical calculations and electronic absorption spectroscopy, and vibrational spectra of the biradicals, which may give rich structural information, have yet to be observed. In this presentation, we will present the first observation of vibrational spectra of singlet and triplet cyclopentane-1,3-diyl biradicals.



sbr (singlet): X = OMe

tbr (triplet): X = Me

Fig. cyclopentane-1,3-diyl biradicals

TRIR spectra of 1,3-di-(4-cyanophenyl)-2,2-dimethoxyoctahydropentalene-1,3-diyl (**s r**) and 1,3-di-(4-cyanophenyl)-2,2-dimethyloctahydropentalene-1,3-diyl (**t r**) in the CN stretching region were observed in dichloromethane. The spin multiplicity of electronic ground state of **s r** is known as singlet [4], whereas that of **t r** triplet [5]. The biradicals were generated by photoinduced denitrogation of the corresponding azo-species, and transformed into the stable tricyclooctane-species via the ring-closure process between C1 and C3. The CN stretch frequencies of **s r** and **t r** were 2218 and 2210 cm^{-1}, respectively, while those of the corresponding azo-species were both 2235 cm^{-1}. Downshifts compared to parental azo-species to biradicals are likely to reflect their radical nature because the CN bonds are expected to largely influenced by the radical electrons located in the para-positions of the groups. The larger shift (−25 cm^{-1}) of the triplet biradical (**t r**) than that (−17 cm^{-1}) of the singlet biradical (**s r**) suggests that the radical nature is more significant in the former species than the latter.

References

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Probing Dimerization of 7-Azaindole in Solutions by Femtosecond Raman-Induced Kerr Effect Spectroscopy

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It is well-known that 7-azaindole (AI) in gas-phase and non-polar solvents forms a dimer via cooperative hydrogen bonds. However, the dimerization of AI in some solutions including acetonitrile and CH_2Cl_2 is still less obvious [1]. To clarify the existence of AI dimer in a wide variety of solvents, one effective way is direct observation of cooperative hydrogen-bonding modes of AI dimer by means of a non-resonant spectroscopic technique. In this study, we have used femtosecond Raman-induced Kerr effect spectroscopy (RIKES) to reveal this problem.

Fig. 1 shows the Kerr transient of AI solutions and their neat solvents of (a) CCl_4 and (b) DMSO. Previously, we have confirmed the dimer formation of AI in nonpolar CCl_4 by a RIKES study [2]. The long time part over 3 ps is characterized by a multi exponential function, except for neat CCl_4 that shows no orientational dynamics. The slowest relaxation time constants for AI/CCl_4 and AI/DMSO are 39 and 30 ps, respectively. Since the shear viscosities (η) of neat CCl_4 and DMSO are 0.91 and 1.99 cP, respectively, the simple Stokes-Einstein-Debye hydrodynamic model ($\tau \propto V\eta$) indicates that the volume (V) of the observed substance for the diffusive relaxation process in AI/DMSO is ca. 2.8 times smaller than that in AI/CCl_4. In this conference, we will show and discuss the low frequency Kerr spectra of AI solutions of CCl_4, $CHCl_3$, CH_2Cl_2, acetone, acetonitrile, and DMSO.

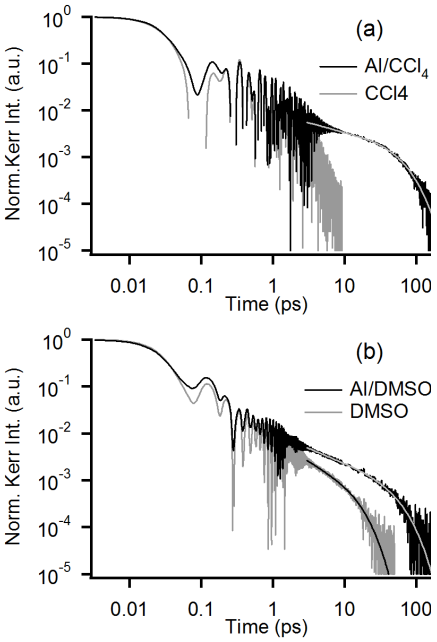

Fig. 1. Kerr transients of AI solutions and neat solvents of (a) CCl_4 and (b) DMSO. Multi-exponential fits are also shown.

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Like-charge ion pairing in aqueous guanidinium chloride solution addressed by ultrafast optical Kerr-effect (OKE) spectroscopy

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The guanidinium cation is the most valuable agent for protein unfolding but both the mechanism by which it interacts so specifically with proteins, and that by which it forms high concentration aqueous solutions, are unclear. However, recent reports of like-charge stacking in solution observed in MD simulations [1] have stimulated experimental studies.

Aqueous guanidinium chloride (GdmCl) solution presents near-complementarity when studied by DRS and optical Kerr-effect spectroscopy in that the former is only directly sensitive to orientational motions of the water molecule, whereas OKE is dominated by orientational motions of the, symmetric but polarizable, cation. DRS studies [2] show, intriguingly, that while viscosity increases strongly with concentration, the water rotational-relaxation timescale remains effectively constant.

Here we will present concentration- and temperature-dependent OKE measurements on GdmCl solution (Fig. 1) that demonstrate that rotational relaxation of the Gdm^+ cation is also fundamentally decoupled from viscosity. In addition, the data show a surprising *reduction* in the heterogeneous character of orientational relaxation at higher concentrations inconsistent with the formation of clusters.

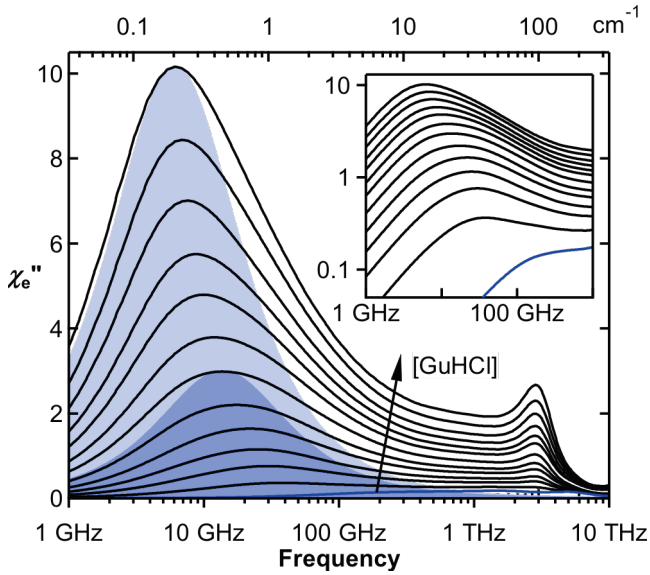

Fig. 1 The OKE spectrum for aqueous GdmCl solution (at concentrations up to 7.4 M) is dominated by reorientations of the Gdm^+ ion. The Debye lineshape is shown in blue to reveal the anomalous broadening of the relaxation band.

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When do ions accelerate or retard water dynamics ?

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There are fundamental and not yet fully resolved questions concerning the impact of solutes, ions in particular, on the structure and dynamics of water, which can be formulated as: Are the effects of ions local or long-ranged? Is the action of cations and anions on water cooperative or not? Here, we investigate how the reorientation and hydrogen-bond dynamics of water is affected by ions in dilute and concentrated aqueous salt solutions. By combining simulations and analytic modeling, we first show that ions have a short-ranged influence and that depending on their interaction strength with water, they may accelerate or slow down water dynamics. A simple additive picture combining the influences of the cations and anions is found to provide a good description in dilute solutions. Deviations from the linear behavior in concentrated ionic solutions are shown to arise from overlapping hydration shells and from an additional collective crowding effect which increases the solution viscosity. This effect is not ion-specific and explains why all concentrated salt solutions slow down water dynamics. Our picture also reconciles the seemingly contradictory experimental results obtained by ultrafast infrared and NMR spectroscopies and suggests that there are no long-ranged cooperative effects in dilute solutions.

Hydrogen bond dynamics in supercooled water: Frequency dependent specific heat and emergence of correlated dynamics

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Molecular origin of the well-known specific heat anomaly in supercooled liquid water is investigated by using extensive computer simulations and theoretical analyses. A rather sharp increase in the values of isobaric specific heat with lowering temperature and the weak temperature dependence of isochoric specific heat in the same range are reproduced in the simulations. We examine the frequency dependent specific heat and calculate the spatio-temporal correlation among temperature fluctuations. These analyses reveal the emergence of temporally slow, spatially long ranged large temperature fluctuations at low temperatures. The temperature fluctuation time correlation function (TFCF) can be fitted to a William-Watts stretched exponential form with the stretching parameter close to 0.6 at low temperatures, indicating highly non-exponential relaxation. Temperature dependence of the relaxation time of the correlation function can be fitted to Vogel-Fulcher-Tamermann (VFT) expression which provides a quantitative measure of the fragility of the liquid. Interestingly, we find that the rapid growth in the relaxation time of TFCF with lowering temperature undergoes a sharp crossover from a markedly fragile state to a weakly fragile state around 220 K.

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Mechanism of photosynthetic water oxidation as studied by flash-induced FTIR difference and time-resolved IR spectroscopies

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Photosynthetic oxygen evolution by plants and cyanobacteria is performed by water oxidation at the Mn_4CaO_5 cluster in photosystem II. The reaction proceeds via a light-driven cycle of five intermediates called S_i states (i = 0–4). In spite of the significance of this reaction for sustenance of life on earth, the details of the reaction mechanism remain unresolved. In this study, we have investigated the molecular mechanism of photosynthetic water oxidation using FTIR difference and time-resolved IR spectroscopies.

Water oxidation reactions in the S-state cycle were monitored by flash-induced FTIR difference spectroscopy [1]. Observed spectra provided information on the structural changes of proteins and substrate water between the S-state intermediates. The proton and protein dynamics during water oxidation were further studied using time-resolved infrared spectroscopy [2]. The time courses of the absorption changes at 1400 and 2500 cm^{-1}, which represent the movements of carboxylate groups and protons, respectively, were monitored upon flash illumination. The results provided insight into the proton-coupled electron transfer processes during individual S-state transitions. In particular, experimental evidence for the proton release before electron transfer during the O_2-evolving $S_3 \rightarrow S_0$ transition was obtained (Fig. 1).

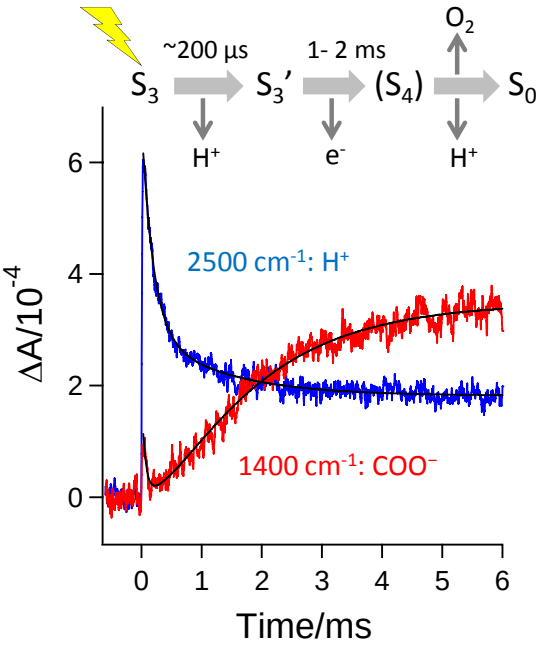

Fig. 1 Time-resolved IR signal during S_3-to-S_0 transition in photosynthetic water oxidaton

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Mechanism of light-driven sodium ion pump

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Light-driven outward H^+ pump bacteriorhodopsin (BR) and inward Cl^- pump halorhodopsin (HR) were discovered from Halophilic archaea 35-40 years ago. Light-driven pumps are used to create membrane potential for ATP-synthesis, and their pump mechanisms have been extensively studied. Since 2000, genomic analysis identified more than 5,000 microbial rhodopsins from marine bacteria, most of which were classified into light-driven H^+ pump (proteorhodopsin; PR). While HR can pump not only Cl^-, but also other monovalent cations such as Br^-, I^- and NO_3^-, microbial rhodopsins can pump only H^+, no other cations. It may be reasonable because the chromophore (protonated Schiff base of all-trans retinal) is positively charged, so that cations cannot stay in the Schiff base region except for the covalently attached H^+. However, we recently discovered light-driven outward Na^+ pump from marine bacteria [1].

The Na^+-pumping rhodopsin, Krokinobacter Rhodopsin 2 (KR2), can also pump Li^+, but it becomes a H^+ pump in KCl and with salts of larger cations. Therefore, KR2 is a compatible Na^+-H^+ pump. KR2 has identical absorption spectra with and without Na^+, indicating that the Na^+-biding site is distant from the retinal Schiff base region. Using ATR-FTIR spectroscopy, we identified the binding site at the extracellular domain. KR2 can be converted to uni-functional Na^+ and H^+ pumps by mutations. These findings demonstrate that the light-driven Na^+ pump is exploited in nature, and we will present the molecular mechanism of light-driven Na^+ pump studied by various methods including time-resolved FTIR spectroscopy.

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Proton transfer reactions and structural changes of the optogenetic protein channelrhodopsin-2 traced by time-resolved step-scan FTIR spectroscopy

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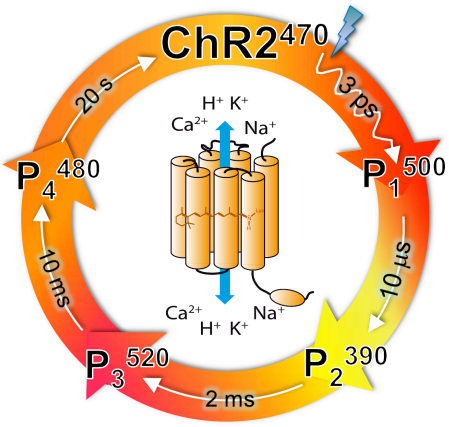
It always was a dream to control cells and living animals by light. The discovery of channelrhodopsin turned the dream into reality as this light-activated cation channel is able to elicit action potentials with unprecedented spatial and temporal resolution. Here, we have traced the structural changes of channelrhodopsin-2 (ChR2) by time-resolved FT-IR spectroscopy using the step-scan technique. For the first time, we have resolved the vibrational changes associated with the open states of the channel (P_2^{390} and P_3^{520}) and characterized several proton transfer events. Analysis of the amide I vibrations suggests a transient increase in hydration of transmembrane α-helices with $\tau_{1/2}$ = 60 µs) which tally the onset of cation permeation. Aspartate 253 accepts the proton released by the Schiff base ($\tau_{1/2}$ = 10 µs), the latter being reprotonated by aspartic acid 156 ($\tau_{1/2}$ = 2 ms). The internal proton acceptor and donor groups, corresponding to D212 and D115 in bacteriorhodopsin, are clearly different to other microbial rhodopsins indicating that their spatial position in the protein was relocated during evolution. Previous conclusions on the involvement of glutamic acid 90 in channel opening are ruled out by demonstrating that E90 deprotonates exclusively in the non-conductive P_4^{480} state. Our results merge into a mechanistic proposal that relates the observed proton transfer reactions and the protein conformational changes to the gating of the cation channel. Our results will not only contribute to improve the properties of this optogenetic tool but will also help in elucidating the temporal sequences of ion channeling across the cellular membrane.



Catalysis of small GTPases by their G-Activating Proteins (GAPs) analyzed by time-resolved FTIR spectroscopy

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Time-resolved-FTIR-difference-spectroscopy monitors reactions mechanisms of proteins at atomic detail (1). Spatial resolution is provided in addition by combination with x-ray structure analysis and biomolecular simulations (QM/MM). The role of catalytic important protein-bound water molecules for proton transfer is elucidated for microbial rhodopsins, bacteriorhodopsin and channelrhodopsin (2,3). Furthermore the GTPase mechanism of the protooncogen Ras is analysed. This protein switch is down regulated by catalysis using GAP proteins. Oncogenic mutations in Ras prevent this catalysis and results in cancer. The Ras-GAP catalysis is resolved at atomic detail (4,5). In order to investigate the protein interactions closer to physiological conditions the ATR (attenuated total reflection) technique is applied (6). This approach is extended to other GTPases, Ran, Rap, Rho and especially Rab (7). The results provide a detailed insight, how small GTPases are regulated by their respective GAPs and provide detailed insight in the dynamics of the active center of this protein-protein interaction.

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Ultrafast Dynamics of Specific Interactions in Photoacid-Base Complexes

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Specific solute-solvent interactions are typically localized and directional with respect to a particular pair of interacting molecules. Classical examples of directional solute-solvent interactions are hydrogen-bonding and charge-transfer interactions, which result from the overlap of occupied and unoccupied donor-acceptor molecular orbitals. Accurate descriptions of these fundamental interactions and their correlation with spectroscopic observables usually require anisotropic quantum chemistry models beyond continuum electrostatics [1,2]. Here, we use 1- and 2-naphthol (1N and 2N) in the electronic S_0 and S_1-states in various solvents, as prototypical photoacids with specific interactions. Using different halocarbon solvents, we observe a substantial lifetime shortening of the S_1-states of 1N and 2N to picosecond time scales, as probed by time-resolved fluorescence and femtosecond UV/IR pump-probe spectroscopy. We ascribe the life-time shortening to deactivation channels following (partial) electron transfer from the photoacid to the solvent. In particular the O-H stretching mode provides direct insights into charge flow upon electronic excitation of the photoacid-base complexes, as well as a probe of dynamics in the electronic excited state. We correlate the O-H stretching frequency shifts to the electronic nature of the O-H groups in specific electronic states by using a perturbative theoretical model originally developed by Pullin, and augmented by the van der Zwan-Hynes relationship [1,2], parametrized with *ab initio* quantum chemistry calculations at the (time-dependent) density functional theory (TD)-B3LYP/TZVP level.

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Ultrafast Charge Generation in Novel Push-Pull Polymers

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Push-pull polymers form the third generation of functional polymers for organic photovoltaic designed on basis of alternating donor and acceptor units [1]. Characteristic for these polymers is the formation of an intramolecular ground-state charge transfer complex and, consequently, a narrow band gap and an increased absorption in the red part of the solar spectrum. Despite impressive efficiencies demonstrated by devices based on these novel polymers [2], very little is known about the crucial steps of charge generation which initiate photon-to-voltage conversion.

Here we study the intricate interplay between the *intra-* and *inter*-molecular charge transfer processes following photon absorption. To distinguish between the two processes, blends of [70]PCBM with two polymers (PCDTBT and BTT-DPP) having different donor-acceptor LUMO energy level offsets were used (Fig.1). Both pristine polymers show a relatively fast (tens of ps) intramolecular recombination of the generated charges as probed by monitoring the polaron absorption [3] (Fig.1, black symbols), leaving hardly any long-lived charges. For the small offset BTT-DPP polymer this situation does not change drastically upon blending with [70]PCBM (Fig.1b). In contrast, blends with the larger offset polymer PCDTBT show a signal growth in the first 2 ps (Fig.1a) assigned to exciton diffusion to the interface. Furthermore, the long-lived component increases 5-fold as compared to the pristine polymer. These observations are consistent with an enhanced intermolecular charge separation in PCDTBT blends, driven by the 0.7 eV offset.

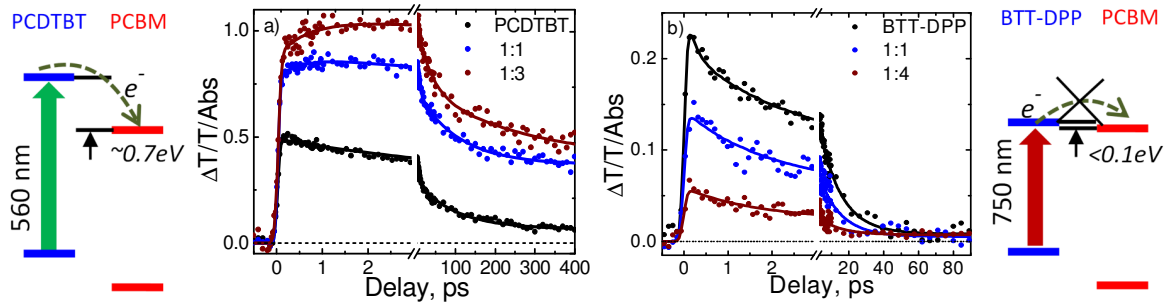

Fig. 1. Transient polaron absorption (probed at 3μm) for PCDTBT (a) and BTT-DPP (b) push-pull polymers, and their blends with different polymer:[70]BPCM mass ratio. All transients are normalized to the amount of absorbed photons. The schematics of the energy levels are shown at the right and left.

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Probing Organometallic Photochemistry in Conventional and supercritical Fluids using time-resolved IR

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We will highlight how fast time-resolved IR Spectroscopy (TRIR) is a powerful tool for probing the structure and reactivity of excited states, as well as the characterization of reactive intermediates and the elucidation of reaction mechanisms in both conventional and supercritical fluids. In particular we will focus on probing the C-H Activation of alkanes using metal catalysts and how spin states affect organometallic reactivity. This lecture will present recent unpublished results in both of these areas.

We have previously probed the factors which govern the C-H activation reaction by elucidating reaction of complexes such as Tp'Rh(CO)$_2$ and Cp'Rh(CO)$_2$ [1,2]. These two reactions show that the nature of the alkane governs these reactions in different ways. Monitoring Spin Changes in the Photochemistry of Fe(CO)$_5$ is a fundamental question, which is key to many areas of inorganic chemistry and this has been the subject of interest for more than 30 years [3]. IR experiments on Fe(CO)$_5$ in n-hexane, and supercritical argon (scAr) and xenon (scXe) have allowed the dynamics of the to be probed particularly by monitoring the conversion of ^{3}Fe(CO)$_4$ to ^{1}Fe(CO)$_4$(solvent) [4].

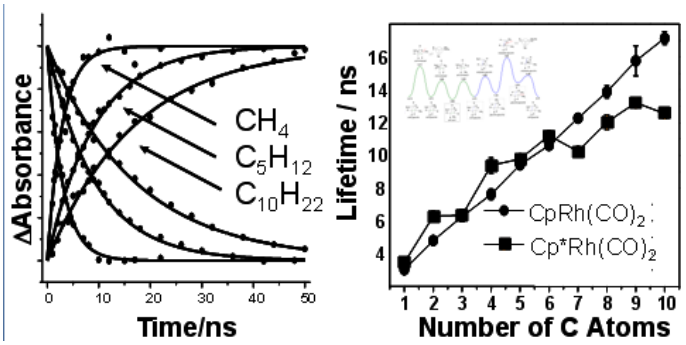

Figure 1 Showing the effect of alkane on the decay of Cp'Rh(CO)(alkane) and the formation of Cp'Rh(CO)(alkyl)H

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Oral Presentation
Friday

"Making the Molecular Movie": Direct Observation of Atomic Motions Involved in Mode Coupling Along Reaction Coordinates

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One of the grand challenges in science is to watch atomic motions as they occur during structural changes. In the fields of chemistry and biology, this prospect provides a direct observation of the very essence of chemistry and the central unifying concept of transition states in structural transitions. This experiment has been referred to as "making the molecular movie". Due to the extraordinary requirements for simultaneous spatial and temporal resolution, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a gedanken experiment. With the development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been realized (Siwick et al. Science 2003). Previously thought intractable problems in attaining sufficient brightness and spatial resolution with electron sources, with respect to the inherent electron-electron repulsion or space charge broadening, has been solved. With this new level of acuity in observing structural dynamics, there have been many surprises and this will be an underlying theme. Several movies depicting atomic motions during passage through structural transitions relevant to condensed phase dynamics will be shown as examples to illustrate the evolution in source brightness (Eichberger et al Nature 2010, Jean-Ruel et al. J. Phys. Chem. A 2011, Gao et al in press 2013). With respect to molecular reaction dynamics, one of the key issues is how chemistry reduces to a few key modes in propagating the system through the transition state. Given the enormous number of possible nuclear configurations, the reaction coordinate is formally an extremely highly dimensional problem; yet there is a tremendous reduction in configuration space at the barrier crossing region. Recent results on photoinduced charge transfer processes in the charge ordered material EDO-TTF shows that the process is slaved by the lowest frequency mode most strongly coupled to the reaction coordinate, that defines the temporal window between inertial and Brownian motion/collision limits. These results provide new insights into this reduction in phase space and how chemical mechanisms lead to transferrable constructs for guiding synthesis. The problem is even more intriguing for biological systems in which there are even more nuclear degrees of freedom, where a similarly enormous reduction in dimensionality occurs. These latest developments in electron source brightness, now capable of providing atomically resolved dynamics for even weakly scattering organic systems, will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules — the fundamental molecular basis of biological systems

Energy transfer in phosphatidylcholine lipid bilayer membranes examined by picosecond time-resolved Raman spectroscopy

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Chemical reactions are affected by the properties of the reaction media. A number of biochemical reactions proceed at lipid bilayer membranes that form quasi-two-dimensional space with a thickness of two lipid molecules. It is therefore important to examine the properties of the lipid bilayer membranes for understanding the biochemical reactions. We estimate the viscosity inside a phosphatidylcholine lipid bilayer by picosecond time-resolved fluorescence spectroscopy [1]. In this study, we examine the thermal property of the phosphatidylcholine lipid bilayers with picosecond time-resolved Raman spectroscopy.

Raman bands of the S_1 state of *trans*-stilbene serve as a picosecond thermometer [2]. Stilbene molecules are solubilized in liposome lipid bilayers for the time-resolved Raman measurements. The liposomes, with a diameter of 100 nm, are prepared by a single phosphatidylcholine, DLPC (C12), DPPC (C16), or egg-PC. DPPC takes the gel form at room temperature while DLPC and egg-PC take the liquid crystal form. The S_1 state of *trans*-stilbene is prepared by the pump pulse at 300 nm. Vibrational cooling process of S_1 *trans*-stilbene is monitored with the probe pulse at 590 nm [3].

Vibrational cooling rate constants of S_1 *trans*-stilbene that is solubilized in DLPC, DPPC, and egg-PC range between 0.09 and 0.11 x 10^{12} s^{-1}. They are similar to the values observed in alkanes. The vibrational cooling rate constant in ordinary molecular solvents shows a good correlation with the thermal diffusivity of the bulk solvent [3]. The effect of water, which has thermal diffusivity 1.6 times larger than alkanes, is limited on the energy transfer in the liposome lipid bilayers. The vibrational cooling rate constant observed in the gel form lipid bilayer membrane is smaller than the rate constants in the liquid crystal form membranes. We suggest that the thermal diffusivity in the gel form lipid bilayer membrane is smaller than the thermal diffusivity in the LC phase lipid bilayer membrane.

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Dynamics of molecular systems probed by IR-induced conductivity

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Many organic and biological macromolecular systems like conjugated polymers, molecular crystals, photochromic proteins, or ionic membrane channels can be integrated into macroscopic electrical circuits using electrochemical cells or by developing an organic/protein monolayer diode structure [1]. In the latter case, the transmitted current can be used as a reporter for their structure and functionality, provided that the current flux is coupled to the local electronic or/and vibrational modes. This concept enables the study and control of the structure, dynamics, and conductivity of macromolecular systems by measuring changes in electric current that result from an optical excitation (‘push’) with IR light.

To study the coupling between conductivity and optical IR excitation we have developed an IR-push -- photocurrent probe technique [2]. We applied this technique to a wide range of molecular systems, including plastic photovoltaic cells and organic monolayer based diodes (Fig.1, top). For photovoltaic cells [2,3] the excitation with IR light leads to the promotion of charges to delocalised states. Although such states are extremely short-lived (<1ps), their excitation enables the charges to overcome the Coulomb attractive interaction and to become separated.

We also observe a strong change of the conductivity after excitation with IR light in the spectral region of C-C vibrational modes at ~1400-1600 cm^{-1} (Fig 1, bottom). The physical phenomena underlying this effect are currently under investigation.

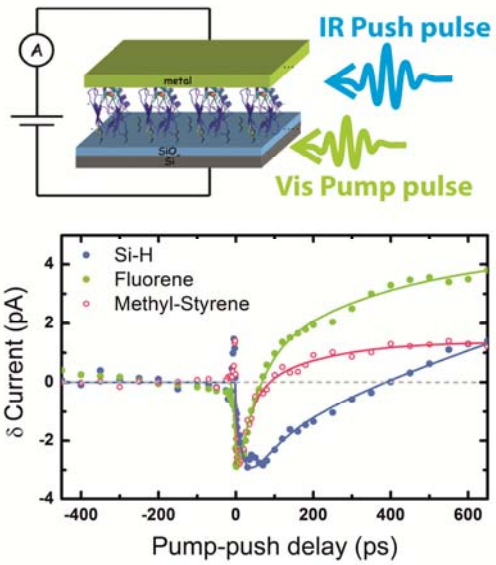

Fig. 1. The concept and experimental results of IR-push - photocurrent-probe spectroscopy for different organic monolayer diodes.

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Control of multipath interference in vibrational excitations for anharmonically coupled oscillator systems

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Coherent control is a technique that manipulates interference of wave functions by adjusting their amplitudes and phases. The pulse shaping technique in mid-IR may open a way toward coherent control of vibrational states of molecules at electronic ground states [1]. Such control may serve for reaction controls, novel information processing, enhancing specific peaks in multidimensional spectroscopy, etc [2-4]. So far the mid-IR pulse shaping has been applied to ladder climbing of a single vibrational mode [5]. We applied the technique to controlled excitations of multiple vibrational modes: the multipath interferences, which form the basis for any coherent control schemes, were manipulated for coupled oscillator systems [6]. Here we extend the work to study the improved pulse design for higher excitation efficiency, the impact of coherence transfer, and the variation of selective excitations.

The metal di-carbonyls have anharmonically coupled symmetric (S) and anti-symmetric (A) CO stretch vibrations. In each of the compounds, the S and A modes constitute a set of vibrational energy levels including their overtones and combination tones (Fig.1). There exist at least two of the resonant two-step excitation paths into the combination tone: one via the S excited state and the other via the A excited state. By use of the phase shaping of IR excitation pulses, the interference between different excitation paths and the resultant excitation efficiency were controlled. Coherence transfer activates other excitation paths and requires unique pulse design for higher excitation efficiency.

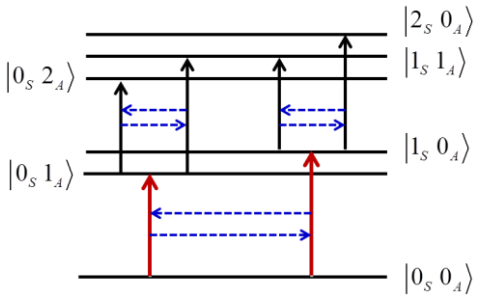

Fig. 1 Energy-level diagram of a coupled oscillator system.

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Vibrational dynamics in the electronically excited state in hydrogen bonding solvents

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In a protic solvent, a solute molecule forms intermolecular hydrogen bonds with solvents if the solute has hydrogen bonding sites such as a carbonyl group. The vibrational dynamics of 9-Fluorenone (FL) in alcohol solutions are previously reported in the electronically ground state and excited states [1, 2]. In this study, we studied effects of hydrogen bond on the vibrational structures and the vibrational dynamics of the CO stretching of the excited state FL in various solvents including alcohol.

In the steady-state IR spectrum, the CO stretching band of FL in methanol-d_4 shows peaks at 1721 cm^{-1} and 1713 cm^{-1}, and a shoulder at 1703 cm^{-1}, which were assigned to free FL, a FL complex with one solvent molecule, and a complex with two solvent molecules, respectively. We measured the visible-pump and IR-probe signals in cyclohexane, acetonitrile-d_3, and methanol-d_4. Figure 1 shows the transient IR spectra of FL in methanol-d_4. The CO stretching band has peaks at (a) and (b), and a shoulder at (c). With the help of quantum chemical calculations, we assigned the bands (a), (b), and (c) to a FL complex with one solvent, free FL, and a complex with two solvents, respectively. The band (b) shifts to the higher frequency side with delay time, and this is probably due to vibrational cooling. Interestingly, the band (a) shifts to the lower frequency side with time. We attribute this shift due to structural rearrangement of the hydrogen-bonded complex of FL and alcohol, which may be influenced by solvation dynamics.

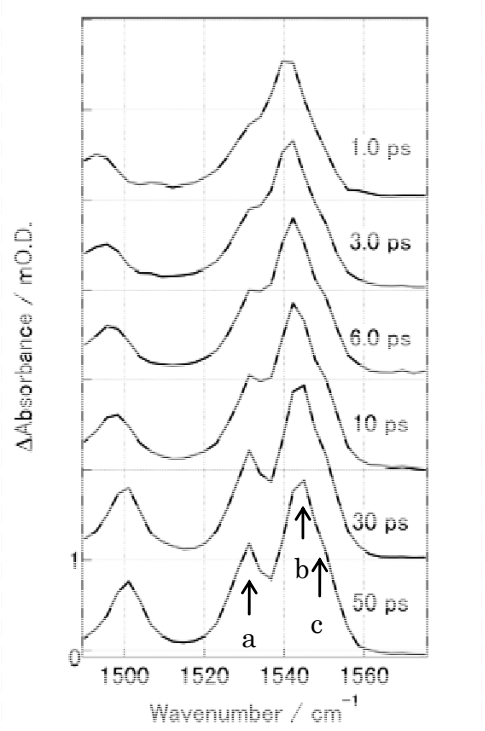

Fig. 1 Transient absorption spectra of FL in methanol-d_4 after excitation at 400 nm.

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Ultrafast photoisomerization of Pfr phytochrome studied by time-resolved infrared and Raman spectroscopy

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Photoisomerization of a protein bound bilin is the initial step of the light sensing and signaling response of photoreceptor phytochrome. In this study, we investigate the ultrafast E-to-Z photoisomerization of the C_{15}=C_{16} methine bridge in phycocyanobilin (PCB) in the Pfr state of cyanobacterial phytochrome Cph1 using a combination of femtosecond stimulated Raman spectroscopy[1] and polarization-resolved femtosecond visible pump infrared probe spectroscopy (prfs VIS-IR).[2] Our integrated IR-Raman approach provides a very detailed picture of the chromophore structure during the photoreaction. Transient stimulated Raman data were collected using a combination of 790 nm Raman pulse (~4 ps) and a broadband probe (830-1000 nm) after triggering the photo-reaction by a 720 nm pulse while maintaining ~90 fs temporal precision. The ultrafast photoexcitation is first dominated by a 10 cm^{-1} red shift of the localized $\nu(C_{15}=C_{16})$ stretching vibration and the 20 cm^{-1} shift of the intense hydrogen out-of-plane (HOOP) mode with a time constant of about 0.4 ps. The prfs VIS-IR experiments on the Cph1Δ2 samples, excited at 715 nm (~ 250 fs IRF), reported absolute orientation of the C_{19}=O transition dipole in the ring D changes on a time scale of about 0.7 ps, thereby indicating already facile rotational dynamics about the C_{15}=C_{16} bond within 1 ps. The intensity decay of both the HOOP mode in FSRS spectra and the concomitant loss of $\nu(C_{19}=O)$ carbonyl vibrational feature in its electronic excited state is interpreted as the formation of the Lumi-F state with a unique C_{19}=O vibration at 1725 cm^{-1}. Our results set a lower limit on the E-to-Z excited state photoisomerization timescale of 0.4 ps - 0.7 ps, and clearly show a ground state photoproduct formed after 4 ps.

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Inter-molecular Coherent Vibration in Oligomers of Gold(I) complex

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Oligomers of dicyanoaurate, ($[Au(CN)_2^-]$), have been known to form strong inter-molecular Au-Au bonding with photo-excitation of the $p_z\sigma \leftarrow d_z\sigma^*$ transition [1]. Structural dynamics involving the bond formation of excited-state oligomers $[Au(CN)_2^-]_n$ in aqueous solutions was studied using picosecond/femtosecond time-resolved emission and absorption spectroscopy [2]. With selective excitation of the trimer ($[Au(CN)_2^-]_3$), transient absorption due to the excited-state trimer was observed around 600 nm (Fig. 1). This transient exhibited a significant intensity increase (τ = 2.1 ps) with a blue shift in the early picosecond time region. DFT/TDDFT calculations revealed that the observed spectral changes are ascribed to the structural change from the bent structures to linear staggered one in the triplet excited-state trimer. The transient absorption also exhibited a clear modulation of the peak position, reflecting coherent nuclear wavepacket motion induced by photoexcitation (Fig.1, inset). The frequencies of the coherent motions are 66 and 87 cm^{-1}, in excellent accord with the frequencies of two Au-Au stretch vibrations in the excited state of the trimer calculated by DFT. Time-resolved emission spectra in the subnanosecond time region showed that association of the excited-state trimer with the ground-state monomer proceeds with τ = 2.0 ns, yielding the excited-state tetramer.

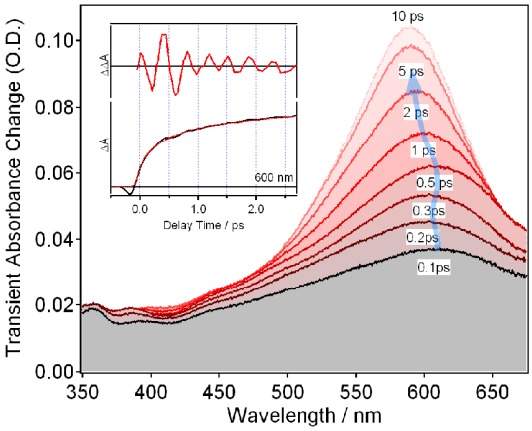

Fig 1. Femtosecond time-resolved absorption spectra of a $K[Au(CN)_2]$ aqueous solution in the time region of 0.1 – 10 ps. The arrow denotes modulation of the transient absorption peak. Inset shows the time-resolved absorption signal at 600 nm. (0.28 mol/dm^3, λ_{ex} = 310 nm)

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Semiquantal wave packet molecular dynamics simulation of hydrogen-bond dynamics in water

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Molecular modeling of quantum effect in hydrogen-bond energetics and dynamics is a fundamental open problem relevant to broad areas of chemistry, biochemistry, and materials science. Nevertheless, real-time and real-space dynamic simulation with realistic molecular models has been hindered by difficulties in dealing with many-body quantum effects in disordered soft-condensed systems. In recent years, we have been developing a semiquantal wave packet simulation method with an emphasis on computationally robust and efficient implementation of realistic molecular dynamics simulation. The method is similar to the thawed Gaussian wave packet but is distinguished by the extended Hamiltonian formalism for both the center and width degrees of freedom which enables stable symplectic propagation. We will first briefly introduce the theory with applications to a simple system-bath model and the Lippincott-Schroeder model of hydrogen-bond [1]. These demonstrate its applicability to problems of wave packet squeezing due to interaction with external degrees of freedom and the subtle geometric isotope effect on hydrogen-bond structure. Next we present recent results of wave packet molecular dynamics simulation for hydrogen-bond exchange and fluctuation dynamics in water [2,3]. The molecular jump mechanism of hydrogen-bond exchange dynamics [4] and the local hydrogen-bond number fluctuation will be discussed. Finally, we make a few remarks on a future direction toward combining nuclear and electron wave packet methods in which the fermion antisymmetry of the latter is treated by the nonorthogonal valence-bond theory [5,6].

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Poster Presentation
Monday

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New Methods in Mixed Electronic-Vibrational Coherent Multidimensional Spectroscopy: Triple Sum Frequency CMDS and Application

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We present a new multiresonant coherent multidimensional spectroscopy (CMDS) technique employing a pathway that is both fully coherent and necessarily unique. This technique is based on a Triple Sum Frequency (TSF) coherence pathway with three excitation pulses having frequencies ω_1, ω_2, and ω_3, and the phase matching condition $k_1+k_2+k_3$. The k_1 and k_2 pulses excite vibrational resonances while the k_3 pulse induces a Raman transition to create a visible output (Fig. 1a). This technique separates fundamental and overtone/combination band states uniquely onto the ω_1 and ω_2 axes. Neat benzene serves as a model system to demonstrate TSF CMDS (Fig. 2). Benzene's inversion symmetry imposes explicit selection rules that demonstrate cleanly the alternating parity of states selected for on each axis, such that one is reflective of an infrared spectrum and the other a Raman spectrum at higher frequencies. Interesting features of benzene are noted such as the surprisingly long lifetime of the ν_{13} C-C stretch overtone and the strong coupling to the *gerade* C-H stretch. Dynamic Stark effects are also observed and modeled and their manifestation in the spectra will be discussed. [1]

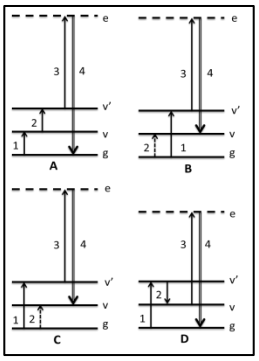

Figure 1: Wave Mixing Energy Level Diagrams for (a) TSF, (b,c) DOVE-IR, and (d) DOVE-Raman CMDS.

Mixed electronic-vibrational CMDS is appealing as a contribution to selectivity for important chemical species with distinct electronic states, such as conjugated moieties and transition metals with low-lying d->d transitions. The former has been explored to some extent in the form of Doubly Vibrationally Enhanced Four-Wave Mixing (DOVE-FWM).[2,3] In DOVE-FWM, infrared transitions directly excite one overtone or combination band state as well as one fundamental state (Fig. 1b,c) or a Raman transition (Fig. 1d). The final interaction is a visible pulse interacting with a (to date virtual) electronic state to induce a Raman output in the visible. *Klug et al.* have had success using DOVE signatures of the aromatic amino acids (as well as two others) in protein identification, and their greater success with organics with low-lying electronic states indicates the resonant enhancement arising from the visible interaction, despite its large detuning (800 nm). Progress toward further employment of these techniques to biochemical systems will be discussed.

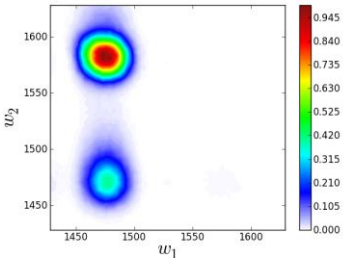

Figure 2: TSF scan of benzene.

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Early steps in the uncaging reaction of NVOC protected puromycin

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NVOC is a photolabile protecting group of the ortho-nitrobenzyl (oNB) type substituted with two methoxy groups, inducing a, in a biological context, valuable bathochromic shift [1]. We want to use puromycin that is protected by a photolabile group of the ortho-nitrobenzyl type to study posttranslational protein folding events.

In order to get a more detailed insight in the mechanism of the uncaging process, which is known to depend strongly on the substituents of the benzene ring, we performed fs-transient absorption measurements in the mid-IR showing the formation of a stabile intermediate within the first few ps after excitation. To our knowledge this is the first time that ultrafast reaction steps on a di-methoxy substituted oNB are being observed. The uncaging reaction is started by exciting the NVOC group with a 350 nm pump pulse preparing the molecule in the singlet S_1 state from where either a ISC to the triplet manifold takes place or a stable aci-nitro intermediate is formed followed by subsequent intramolecular proton transfer reactions. After initial cooling processes product bands appear at 1230, 1460 and 1550 cm^{-1} within the first 10 ps that can be assigned to the aci-nitro intermediate, most likely the aci^{EE} configuration [2]. Additional measurements in the visible range showed a 32 µs time-constant for the uncaging reaction, whereas in a series of FTIR measurements in the range of the CO_2 absorption a yield of 0.013 was found. Furthermore, the puromycin activity has been studied on an assay of firefly luciferase nascent chain complexes showing the release of puromycin after 350 nm excitation.

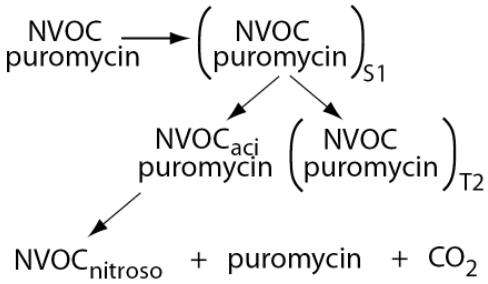

Fig. 1 Generalized reaction meachanism leading to the release of puromycin.

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Mutual Orientation of Reactants in Bimolecular Photoinduced Electron Transfer in Solution

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The predetermined orientation of molecules is an indispensable requirement for the efficient electron transfer (ET) cascade in light harvesting reaction centers. In nature, the optimal orientation is ensured by the protein backbone hosting the chromophoric molecules. In contrast, for unconnected and backbone-free donor-acceptor (D-A) pairs in liquid solution, one expects a random arrangement of the molecules. Therefore theoretical approaches for bimolecular ET treat the shape of the reactants as spheres, assuming that preorientation does not play a role. Nevertheless, also here one could expect a preorientation, since a spherical shape is rare on a molecular level.

To investigate the interplay between D-A pairs during ET on the ps-time scale, we have used ultrafast polarization-resolved Vis-pump mid-IR probe spectroscopy. Herein, D is electronically pumped to the S_1-state and after ET, the vibrational modes of the resulting $A^{\bullet-}$ are probed by mid-IR pulses, polarized parallel and perpendicular to the pump beam. The reconstructed anisotropy contains then information about the angle between the electronic transition dipole moment of D and the vibrational one of $A^{\bullet-}$.

Using this approach, we were able to measure anisotropic behaviour of D-A pairs in solution upon photoinduced bimolecular ET. First experiments of a systematic study showed that the mutual arrangement of the D-A pairs during ET is influenced by the solvent polarity, the free energy ΔG_{ET} as well as the chemical structure of the molecules and does not explicitly require a molecular connection or a surrounding protein shell in order to get preorientation for efficient ET.

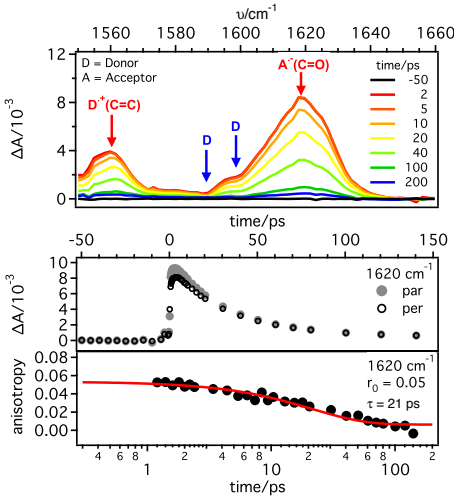

Fig. 1: Transient IR spectra of perylene (D) and phthalic anydride (A) in acetonitrile after 400 nm excitation of D (top) and the time-profile of the polarized transient absorption and of the anisotropy of $A^{\bullet-}$ (bottom).

UV-excited time-resolved HD-VSFG study of the photoionization dynamics of indole at the air/water interface: A vibrational signature of hydrated electrons at the interface

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Hydrated electrons are intensively studied in the bulk aqueous solution as the most fundamental anion species comprised only of electrons and surrounding water molecules. At the interface, however, there are only a few studies about the hydrated electrons, and even their existence in the interface region is still controversial. In the present study, UV-excited time-resolved heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy was developed, and was applied to the air/indole aqueous solution interface with the aim of understanding the fate of the electrons generated at the interface by the photoionization of indole molecules.

In the observed transient $\mathrm{Im}\chi^{(2)}$ ($\Delta\mathrm{Im}\chi^{(2)}$) spectra (Fig. 1), a transient signal with one negative peak at 3200 cm^{-1} and one positive peak at 3500 cm^{-1} was found. Since both peaks appear in the OH stretch region, it is highly likely that they are attributable to the water molecules interacting with electrons (Fig. 2). The appearance of two peaks is in sharp contrast with the transient Raman spectra in the bulk [1] where a transient signal with only one peak at 3200 cm^{-1} is observed. This result is indicative of a unique solvation environment for excess electrons at the interface.

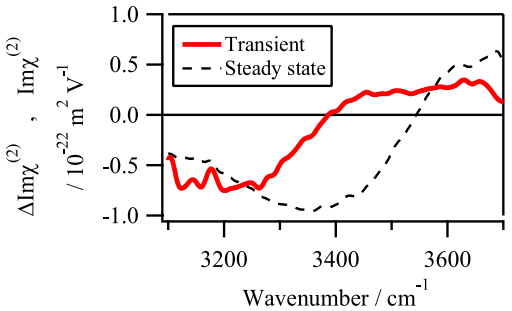

Fig. 1 $\Delta\mathrm{Im}\chi^{(2)}$ spectrum of the air/indole aqueous solution interface at 1 ps delay (solid line), together with the steady-state $\mathrm{Im}\chi^{(2)}$ spectrum (broken line).

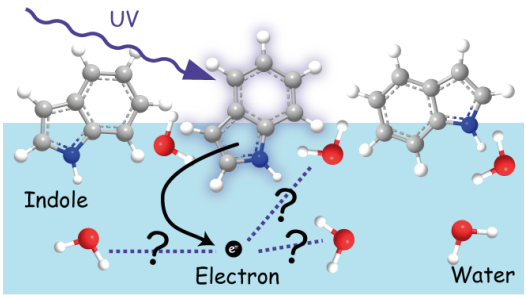

Fig. 2 Figurative sketch showing an electron at the air/water interface generated by the photoionization of indole.

Reference:

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New Methods to Measure Anharmonic Coupling using Femtosecond Stimulated Raman Spectroscopy

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Our lab has been developing new methodologies to measure anharmonic coupling using two-dimensional femtosecond stimulated Raman spectroscopy (2D-FSRS). Fifth-order Raman uses a short impulsive pump pulse to drive low frequency modes into coherence. The high frequency modes are probed using Stimulated Raman Spectroscopy (SRS) at different time delays. However, this signal tends to be contaminated by unwanted third-order cascades that appear at the same frequency and along the same wave vector as the 5th-order signal [1,2]. To overcome these problems, our new 2D-FSRS method acts via a seventh-order polarization in the sample (Fig. 1). In this method, picosecond pulses are used to excite a low frequency modes using a process called spectral focusing.[3] The system is then probed with a SRS pulse sequence at different time delays (T). In this method the signals from the cascades travel along different wave vectors, making it immune to cascade contamination.[4]

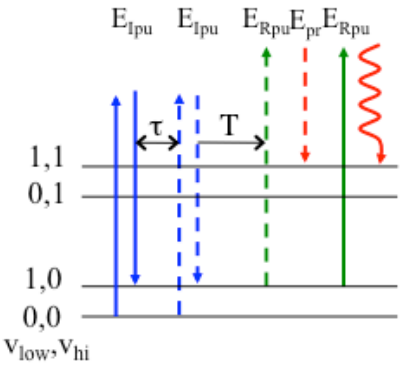

Fig. 1 Wave-mixing energy level diagram for seventh-order 2D-FSRS.

Current experiments have focused on the vibrational population transfer required in the first half of the seventh-order process. Specifically, altering the characteristics of the picosecond pulses, such as amount of applied chirp and power.

In spectral focusing, an instantaneous frequency difference (IFD) is created at different time delay, and when this IFD is resonant with a vibrational mode there is population transfer resulting in an increase in signal in a scan, shown in Fig. 2(a). Figure 2(b) shows the sum of the 2D scan for all wavelengths. The time axis is converted into wavenumbers and the peaks in signal correspond to excitations of the vibrational modes in the sample, chloroform ($CHCl_3$).

Our recent results indicate that seventh-order 2D-FSRS offers promise as the direct Raman analog of current 2D-Infrared spectroscopic methods.

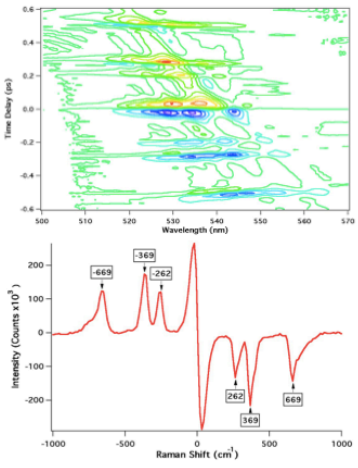

Fig. 2 2D scan and 1D trace of population transfer in chloroform.

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Conformational change of azobenzene-based photoswitchable O*m*PE- foldamer due to photoisomerization

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Foldamers have the ability to adopt defined secondary structures. To achieve time control over the conformational changes of the O*m*PE-foldamers[1], the photoswitch azobenzene was inserted in the backbone of the foldamer 10_5[2]. For *trans*-azobenzene in acetonitrile, an α-helix is formed, stabilized by the polar interactions of the side chains with the solvent and the π-contacts between the phenyl rings. UV light converts azobenzene into the non-planar *cis*-isomer, disturbing the stabilizing interactions and resulting in unfolding of the helix.

Femtosecond transient IR pump-probe-spectroscopy was performed to investigate the dynamics of the unfolding of the foldamer due to *trans*→cis-photoisomerization of azobenzene. By excitation at 325 nm, the dynamics of the absorption changes of the aromatic vibrations (1540-1630 cm^{-1}) as well as the side chain vibrations (1680-1760 cm^{-1}, 1180-1320 cm^{-1}) of the foldamer were studied. The transients of the side chain vibrations show the formation of product absorption bands with a time constant of 30 ps. Based on the results of monomer and foldamer, this time constant can be assigned to the unfolding of the helix.

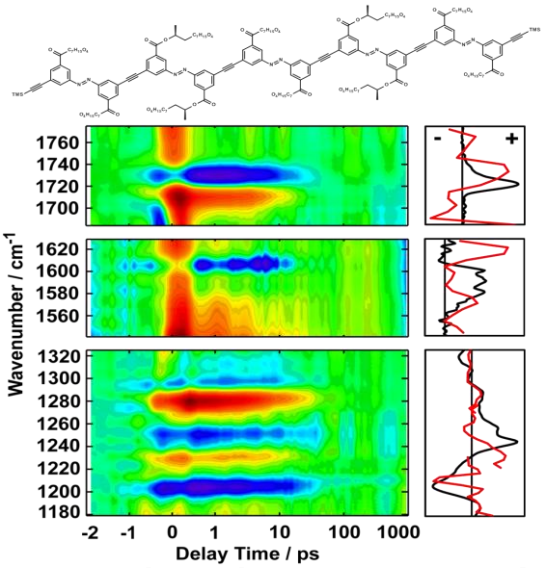

Fig. 1: Chemical structure (top) and time-resolved IR absorption spectra of the foldamer 10_5 (bottom).

References:

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Raman-enhancement mechanism by a nearby plasmonic cluster: the coupling of plasmonic electron motion with vibrational modes of analyte

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Plasmonic nanoparticles have collective electronic excitations and they are expected to be an effective sensitizer for various optical processes. We recently found that plasmonic clusters such as Na_8 and Au_8, much smaller than typical nanoparticles, also show remarkable enchanements for Raman scattering of an analyte molecule, pyrazine [1, 2]. Although the classical electromagnetic (EM) approaches such as the FDTD method give a reasonable explanation for the enhancement from the viewpoint of near-fields generated around nanoparticles, quantum chemical approaches are essential for smaller systems. In quantum mechanics, the Raman scattering probability is expressed as being proportional to the vibrational normal-mode derivatives of the polarizability tensor. Polarizability is related to the transition density which corresponds to the spatial pattern of electronic motion for electronic excitation. Therefore, the mechanism of the Raman enhancement should be understood from the correlation between the vibrational motion of an analyte molecule and the electronic motion of a plasmonic cluster. The correlation is inspected by visualizing the vibrational normal mode derivatives of transition density.

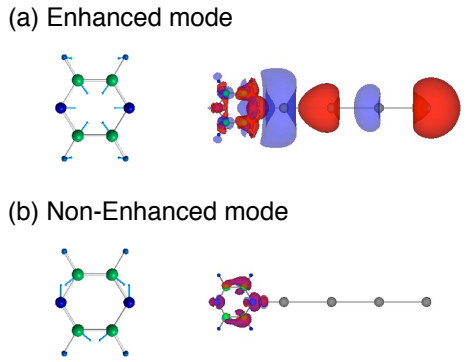

Fig. 1 Pyrazine's normal modes and their coupling with the plasmonic excitation of Na_4.

Figures 1a and b show the vibrational normal-mode derivatives of the transition densities for the enhanced (1557cm^{-1}) and non-enhanced (1260cm^{-1}) modes, respectively. As clearly shown, the enhanced mode is coupled to the global electronic motion. This mode has in-phase motions of H, C and N atoms on the right hand side of pyrazine and is effectively coupled to the plasmonic electron motion along the molecular axis of Na_4. In the same way, we can explain mode dependence of the enhancement, whereas the classical EM theory fails to do.

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Charge Dynamics in Novel Star-Shaped Conjugated Molecules

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Bulk-heterojunction organic solar cells (OSCs), based on solution-processable small-molecular weight donors are a promising alternative to the conventional polymer-based OSCs. Small molecules have a number of advantages such as high purity, excellent batch-to-batch reproducibility, well-defined molecular structure and conjugation length, etc [1]. Due to novelty of such molecules, one of the key phenomena in the OSCs that directly influences overall efficiency of the device - generation of free charges from an initially absorbed photon – has received no attention insofar.

In this contribution, charge generation and recombination processes are studied in blends of three different star-shaped donor molecules (Fig. 1) and a $PC_{70}BM$ acceptor. Charge dynamics were investigated by ultrafast photoinduced absorption spectroscopy using a pump pulse in the visible to mimic the sun photon and IR (2-10 μm) probe pulse to monitor distortions in the molecule backbone caused by generated polarons. We show that in films of pristine star-shaped molecules efficient *intra*molecular recombination of separated charges occurs with a characteristic time of 10 ps (Fig.2). In contrast, at high $PC_{70}BM$ concentrations *inter*molecular electron transfer from $PC_{70}BM$ back to the star-shaped molecule becomes dominant with a longer time scale of 20 ps. The long-time surviving probability of charges depends on the $PC_{70}BM$ concentration, with an optimal ratio of 1:1. These results demonstrate that the star-shaped donors do provide efficient charge separation in the $PC_{70}BM$ blends which makes them perspective donor materials in OSCs.

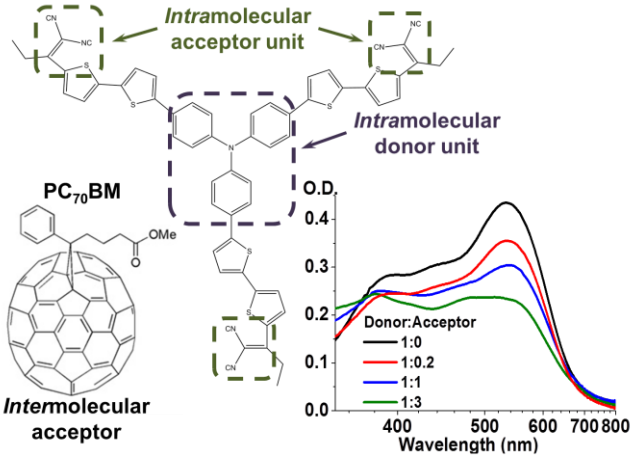

Fig. 1. A typical structure of the star-shape molecule [1], and absorption spectra of blends with different donor:acceptor content. Other SMs differ by a number of thiophene rings (2 or 3) and end chains.

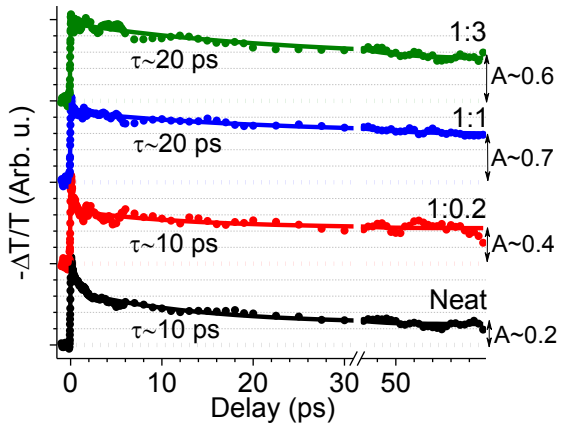

Fig. 2. Representative PIA isotropic transients for films of star-shaped molecules (donor) and $PC_{70}BM$ (acceptor) blends with different donor:acceptor concentrations.

References

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Femtosecond Time-Domain Raman Tracking of the Primary Photoreaction Process of Photoactive Yellow Protein

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Photoactive yellow protein (PYP), which was discovered in *Halorhospira halophila,* is believed to be a blue-light photoreceptor for the negative phototactic response of this organism. The function of PYP is realized by a photocycle, driven by a photoinduced *trans*-to-*cis* isomerization of the embedded chromophore, *p*-coumaric acid (pCA). Although the slower reaction dynamics of this photocycle has been well-characterized, little is known about the dynamics that proceeds on the femtosecond to picosecond time scale, including the mechanism of the photoisomerization of pCA [1]. To gain detailed knowledge about the primary process of the photoreaction of PYP from the structural viewpoint, we carried out time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS [2]).

The obtained data clearly showed rich dynamics in the low-frequency region (<200 cm^{-1}) in the early delay time (<1 ps). Furthermore, a distinct spectral shift was observed for the marker band of the hydrogen-bond strength between pCA and the neighboring amino acid Glu46. On the basis of these observations, we discuss the ultrafast relaxation of the hydrogen-bonding structure, which appears to occur prior to the photoisomerization of pCA.

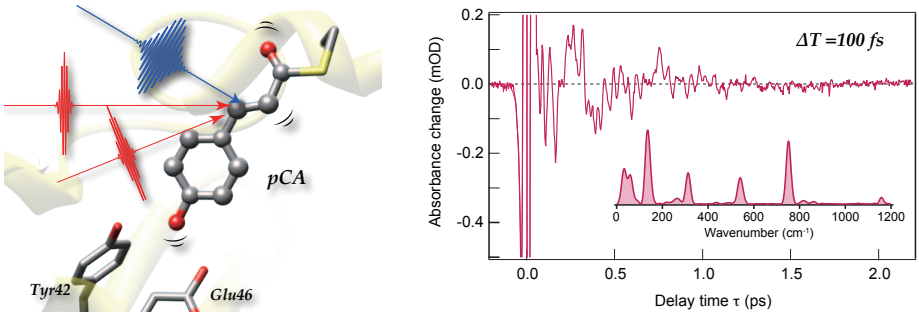

Fig. Schematic representation of the TR-ISRS experiment for PYP (left), and the oscillatory component of the TR-ISRS data for PYP, obtained at ΔT = 100 fs (right). FT power spectrum of the oscillatory component is also shown in the inset.

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Real-Time Tracking of Two Phytochrome Isoforms During Pr Photoisomerization

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Photoisomerization of tetrapyrrole chromophore is the basis of the light sensing and signaling response of phytochrome. Z-to-E photoisomerization of the Cph1Δ2 phytochrome in Pr form has been investigated by polarization resolved femtosecond visible pump-infrared probe spectroscopy, which yields structural information on the Pr excited (Pr*), Pr ground (Pr), and Lumi-R product states. Two photoreaction time constants of (4.7 ± 1.4) and (30 ± 5) ps were found. Rotation of ring D was observed in Pr* with a time constant of 30 ± 5 ps. The polarization resolved signals indicate, that 16% of the excited chromophores reach a 90° twisted transition state after 21 ps.

Two distinct bleaching signals at 1701 cm^{-1} and 1708 cm^{-1} were found. The transient dynamic at 1701 cm^{-1} differs from that at 1708 cm^{-1}. This cannot be explained by an overlap of excited state dynamics at 1680 cm^{-1} and bleaching dynamics at 1708 cm^{-1}. Contributions from a hot ground state were not observed. The orientations of the ring D C=O vibrations agree well with the reported structures of Pr-I and Pr-II.[1] We determined distinct photoisomerization yields of 3% and 29% for the isoforms Pr-I and Pr-II (Fig.1), respectively.

The overall photoisomerization is best explained by a single rotation around C15=C16 methine bridge in the Pr* state and a diffusive interaction with its protein surrounding.[2]

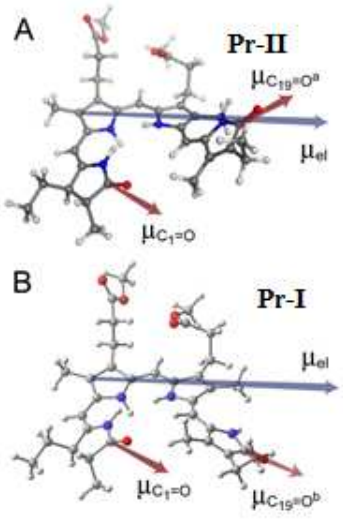

Fig.1 PCB chromophore geometries with Pr $S_0 \rightarrow S_1$ transition dipole moment μ_{el} (black arrow) and vibrational tdms of $\nu(C_{19}=O)^a$ of Pr-II and $\nu(C_1=O)$ (red arrows).

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Salt bridges function as nucleation sites for α-helix folding

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Salt bridges are attractive interactions between oppositely charged side chains that can provide thermodynamic stability to proteins and peptides. [1-2] However, their role in the dynamics of the folding process remains ambiguous. [3-4] Here we use time-resolved infrared (IR) spectroscopy to study the effect of Glu^--Arg^+ salt bridges on the dynamics of α-helix formation. To determine the contribution of salt-bridge interactions, we investigate four alanine-based α-helical peptides in which salt bridges are formed between Glu^- (E) and Arg^+ (R) residues that are spaced either three (*i*, *i*+3) or four (*i*, *i*+4) residues apart, and with the Glu^-/Arg^+ dipole moment either parallel (ER) or antiparallel (RE) to the overall α-helical dipole moment (Fig. 1a). A ns temperature-jump (*T*-jump) initiates α-helical melting, and the equilibration is monitored by probing the transient absorption of the amide I' mode of the peptide backbone. We observe single-exponential relaxation kinetics, indicating that a two-state model can account for the helix-coil transition (Fig. 1b). From a combined analysis of the transient-IR measurements and steady-state UV circular dichroism we determine the folding rates (Fig. 1c). We find that α-helix folding is faster for peptides in which the helix-stabilizing effect of the salt bridge is largest (spaced four residues apart and with the Glu^--Arg^+ dipole moment parallel to that of the α-helix), indicating that salt bridges act as a nucleation site for the folding process.

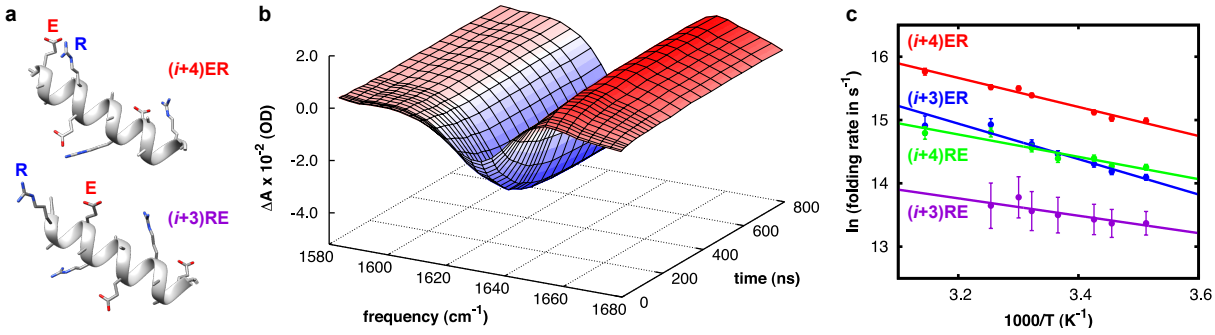

Fig. 1 (a) Schematic representation of the folded structure of two of the peptides. (b) Observed *T*-jump relaxation dynamics of peptide (*i*+4)ER. (c) Arrhenius plots of the folding rates of the investigated peptides (E=Glu^-, R=Arg^+).

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Towards Time-Resolved Host-Guest Chemistry: Charge Transfer Dynamics of Perylene-Macrocycle Complex

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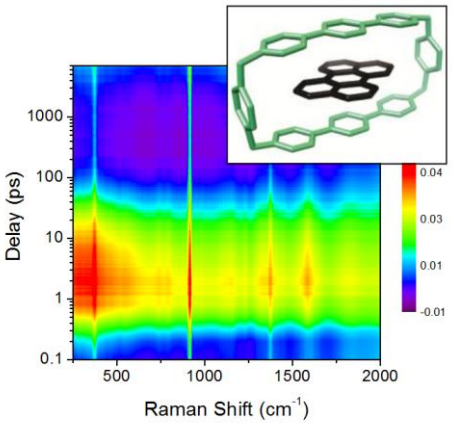
The recently developed macrocylcic PAH scavenger "ExBox^{4+}", comprised of two linked 1,4-phenylene-bridged bipyridinium units, has proven to be quite versatile and strongly complexes to several common chromophores, such as perylene.[1] Here, we use femtosecond stimulated Raman spectroscopy (FSRS) to study the structural dynamics following charge transfer from perylene to the surrounding ExBox^{4+} moiety as a probe of time-dependent host-guest interactions.



After photoinduced charge transfer, a strong time-dependent peak is observed at 1570 cm^{-1} and is attributed to the sum of a weak perylene cation C=C symmetric core stretch and an intense C=N quadrant stretch in the pyridinium portions of the ExBox^{3+} host. This signal rises in ~300 fs and decays in 40 ps, the lifetime of the charge-transfer state. TD-DFT calculations suggest that one of the "extended viologen" sides of the ExBox host undergoes a significant geometry change upon reduction: one phenylene linker becomes co-facial with the surrounding pyridinium units leading to a delocalization and stabilization of the radical. This rotation appears to occur within 300 fs. The intensity of this C=N quadrant mode is enhanced by a factor of ~200 relative to its analogue in ExBox^{4+} due to the change in symmetry from the phenylene rotation induced by charge transfer. We also find that the frequencies of the resonantly-enhanced perylene cation modes all lie near those of the neutral perylene ground state, indicating relatively little structural evolution.

These experiments will also provide a basis for further studies on photo-driven molecular machines currently being developed utilizing this macrocyclic host.

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Structural transformations of liquid water under high pressure conditions: experimental and computational characterization.

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Time resolved vibrational spectroscopy and molecular dynamics simulations (MD) have been used, for the first time, to investigate the structural modifications of liquid water as a function of pressure and temperature. We characterized the pressure dependence (10^{-4} - 0.9 GPa) of the OD stretching lifetime and of the anisotropy decay time in an isotopically-diluted mixture HOD/H_2O (7 %) at 298 K and 363 K using a sapphire anvil cell (SAC). At 298 K the OD stretching lifetime, as a function of pressure, is almost constant till 0.2 GPa, then a clear decrease is observed from 1.8 ps to ~1.4 ps. At 363 K a monotonous decrease is observed from 2.4 ps to ~ 1.4 ps. On the other hand, while the anisotropy decay time at 363 K is constant in the whole inspected pressure range, at 298 K we observed two distinct and well defined trends: the initial fast decrease of the anisotropy decay time, from 2.5 to 1.4 ps, is followed by a constant trend around a value of 1.3 ps.

MD simulations, employing a polarizable force field, have been performed at ambient temperature and at density values corresponding to pressures ranging from 10^{-4} to 0.9 GPa in the NVE ensemble. The pressure dependence of the calculated anisotropy decay time reproduces the experimental behavior and is justified in terms of the structural rearrangements of water molecules. The most important change observed with increasing pressure concerns the progressive merging of the second solvation shell into the first one, giving rise to interstitial water molecules that approach the central molecule without being hydrogen bonded to it.

The mechanism explains the experimental observation and is fully consistent with the idea of continuous structural modifications from low density (LD) to high density (HD) water. The results obtained from experiments and simulations converge to the identification, for the first time, of the “regions of existence” of LD and HD structures of liquid water.

Mid-infrared spectroscopy by chirped pulse upconversion

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The chirped upconversion method combining with a CCD camera detector for detecting mid-IR pulse has been applied to 2D spectroscopy and pump probe measurements in the frequency region above 1800cm^{-1} [1]. Here the upconversion of pump probe transient signals in the lower frequency region below 1800cm^{-1} were measured by using the nonlinear optical crystal AgGaGeS4. This method can also cover the detection window above 2000cm^{-1} frequency region, see figure 1(a).

Use the method we succeeded the detection of the intervalley scattering dynamics of Γ6 → X6/ X7 in thinner GaAs crystal, as shown in figure 1(a). The dynamics of the mid-IR absorption around 1520cm^{-1} is due to the hot electron transition X6→ X7, as consistent with previous experimental result [2]. For weaker transient signal of less than 1milliOD, it was examined with the blue light photoreceptor protein Slr1694. The extracted absorption difference spectrum is shown in figure 1(b), in comparing with the one detected with the traditional MCT detector. The two signals are consistent well at this frequency window. Thus for the first time we realized an important expansion of the application range of this method. This unpconversion method is an attractive alternative to mid-IR detection, enabling the use of cheaper CCD detectors and affording a sampling of hundreds channels instead of the standard 32, 64 or 128 in MCT arrays.

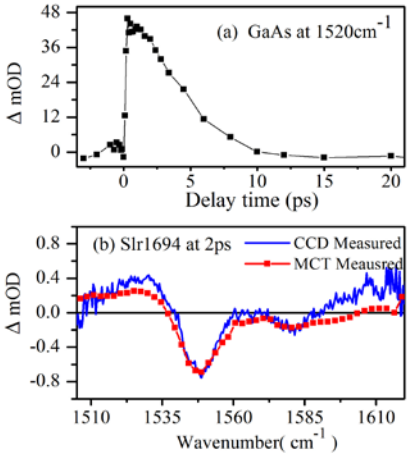

Fig. 1 GaAs and protein Slr1694 mid-IR signals measured by chirped pulse upconversion method.

References:

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Conformational dynamics of fish type III antifreeze protein studied with time-resolved vibrational spectroscopy

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Antifreeze proteins (AFPs) are a class of proteins that are found in the body fluids of organisms that need to survive at sub-zero temperatures. AFPs act as cryoprotectants by lowering the freezing point of aqueous solution with respect to the melting point [1]. A precise molecular picture of the work mechanism of AFPs as well as knowledge about the protein domains involved in antifreeze activity remain elusive.

We performed time- and polarization-resolved pump-probe and two-dimensional infrared (2D-IR) experiments on the amide I-vibrations of a 7 kDa type III antifreeze protein (AFP III, pdb-code: 1HG7). In the pump-probe experiment, we use broadband excitation pulses of ~ 250 cm^{-1} bandwidth and 100 fs duration to excite the complete amide I-region of the protein. The transient spectra show the presence of two spectral components that decay with different lifetimes, indicative of the presence of two distinct amide vibrations. Based on previous work [2], we assign these components to the two IR-active modes (a_+, a_-) that are typically found in beta-sheets of proteins. We also performed 2D-IR experiments to study the coupling between the a_+ and a_- amide modes. The 2D-IR spectra show clear cross-peaks between the two amide modes. The amplitudes of the cross-peaks increase with increasing delay time (see figure), which means that the cross-peak signals result from energy transfer between the two amide modes. This energy transfer takes place on a timescale of ~ 5 ps. This time scale increases when the temperature is decreased. We observe a similar decay time for the anisotropy of the two amide modes, indicating that the energy transfer and the depolarization are both caused by the conformational fluctuations of the beta-sheets of the antifreeze protein.

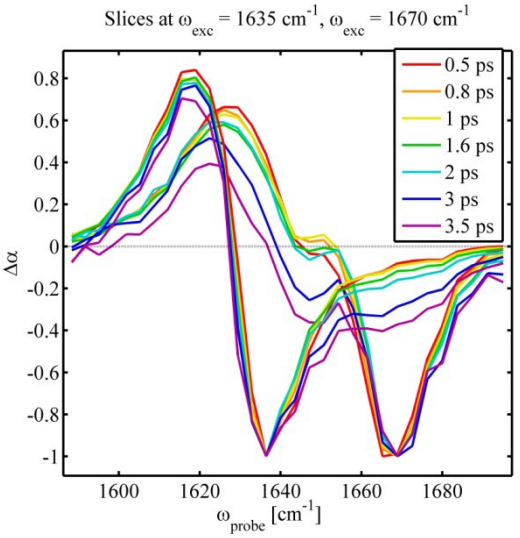

Fig. 1: Cuts of the 2D-IR spectra at excitation frequencies of 1635 cm^{-1} and 1670 cm^{-1}. All spectra are normalized to the maximum absorption change at the two respective excitation frequencies to illustrate the ingrowth of the cross-peak signal at the unpumped vibration.

References:

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Visible pump-IR probe Spectroscopy on Fluorenone and Water-soluble Fluorenone in Solutions

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In water, a solute molecule forms intermolecular hydrogen bonds with water molecules if the solute has hydrogen bonding sites such as a carbonyl group. The hydrogen bonds influence various properties of solute such as its electronic states, molecular structures, and so on. Vibrational structures of solute are also changed by the electronic excitation. 9-Fluorenone (FL) has a carbonyl group which can form hydrogen bonds. The vibrational dynamics of FL in alcohol solutions are previously reported in the electronically ground state and excited states [1, 2]. In this study, we studied effects of hydrogen bond on the vibrational structures and the vibrational dynamics of the CO stretching of the excited state FL in various solvents and water-soluble 9-fluorenone-4-carboxylic acid (FL-4-COOH) in D_2O with NaOD by sub-picosecond visible-pump and IR-probe spectroscopy.

Figure 1a shows temperature dependence of the steady-state IR spectrum of FL-4-COOH in D_2O with NaOD. The CO stretching band shows a peak at 1701 cm^{-1} at 293 K. The COO^- symmetric and antisymmetric stretching bands show peaks at 1404 cm^{-1} and 1565 cm^{-1}, respectively, at 293 K. The symmetric and antisymmetric bands shift to lower and higher frequency sides, respectively. Figure 1b shows the transient IR spectra after the electronic excitation. A bleach at 1561 cm^{-1} may come from the COO^- antisymmetric stretching band. The bands (a) and (c) show upshifts in time and the band (b) shows downshift. The mechanism of this difference will be discussed.

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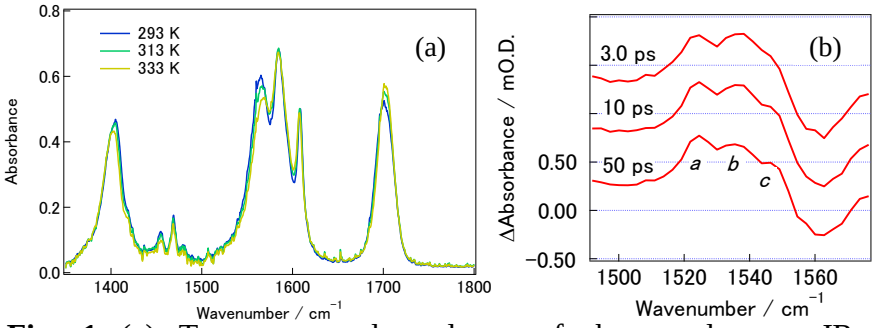

Fig. 1 (a) Temperature dependence of the steady-state IR spectrum and (b) the transient IR spectra after the electronic excitation of FL-4-COOH in D_2O with NaOD.

Laser-induced temperature-jump infrared-spectroscopy to study peptide folding dynamics with site-specific resolution

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The formation of β-sheets plays an important role in protein folding, but also in fibril formation due to their propensity for aggregation. β-hairpin peptides, composed of two antiparallel strands connected by a turn, provide ideal model systems to study a well-defined structure containing a sheet segment. We studied several variants of β-hairpin sequences that are stabilized by Trp-Trp cross-strand interactions using temperature-jump IR spectroscopy and isotopic editing. Rapid heating of the solvent is induced by a Raman-shifted Nd:YAG pulse ($\Delta T \sim 10°C$ in 10 ns) and ns-to-μs peptide dynamics is monitored at single wavelengths using a quantum cascade laser tunable in the amide I region. Isotopic ^{13}C labeling on selected C=O amide positions facilitates dynamics with residue-specific resolution and without perturbing spectroscopic probes. The isotope-edited kinetics support a multistate dynamic behavior being consistent with a hydrophobic collapse hypothesis for the folding process [1-3]. Recently, we studied polyglutamine (polyQ) peptides with different sequence lengths ($K_2Q_nK_2$ with n=10,20,30). PolyQ repeats are found in proteins associated with many neurodegenerative diseases and it is agreed that the length of the polyQ sequence is critical for inducing fibril formation, although the molecular mechanisms are still poorly understood. $K_2Q_{10}K_2$ reveals a temperature-stable random structure. Increasing the peptide length to $K_2Q_{20}K_2$ results in significant fraction of different β-structures, clearly seen in IR bands representative for intra- and intermolecular β-sheets. Our T-jump studies $K_2Q_{20}K_2$ indicate different conformational dynamics for intra- and intermolecular β-structures.

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Transporting a proton with a molecular crane

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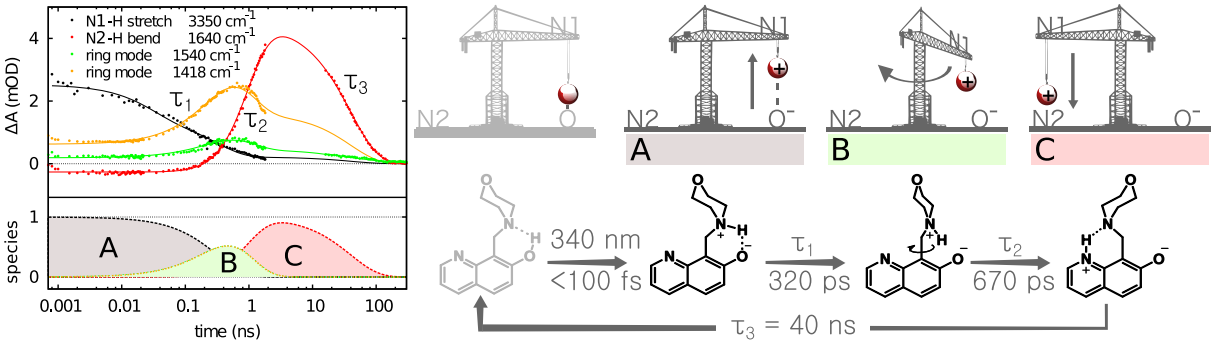
Brownian rotors are ubiquitously employed in nature as molecular machines. The meaning of viscosity at the length scales of these molecular machines is still under debate [1]. Here, we study the mechanical properties of a synthetic rotor, a photo-activated proton crane (see figure) using femtosecond UV-pump IR-probe spectroscopy. Upon electronic excitation a proton is transferred from the hydroxy to the amine group N1, located on a Brownian rotatable morpholino side chain, which delivers the proton to the aromatic nitrogen N2 [2].

The molecular vibrations allow us to study this process in detail. The intensity of the N^+—H stretch vibration is strongly enhanced when H-bonded to O^-, so this mode serves as a marker for the breaking of the $N1^+$—H•••O^- hydrogen bond. The aromatic $N2^+$—H bending mode at 1640 cm^{-1} marks the arrival of the proton at N2. The aromatic ring vibrations also serve as excellent marker modes due to their strong sensitivity to the structural changes during the proton transport.

We find that the proton transport involves multiple timescales: After the <100 fs proton transfer from OH to N1, the $N1^+$—H•••O^- hydrogen bond breaks with τ_1 = 320(11) ps. Secondly, the protonated crane arm rotates with τ_2 = 697(25) ps to deliver the proton at N2. The final species decays with an excited state lifetime τ_3 = 39.81(13) ns. Surprisingly, the rotational dynamics are almost four times slower than predicted from the viscosity and the effective radius of the side group [2].



References:

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Triplet Formation Mechanism in Cofacial Perylene Diimide Dimers Interrogated by Femtosecond Stimulated Raman Spectroscopy

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The aggregation behavior of perylene-3,4:9,10-bis(dicarboximide) (PDI) makes it an ideal compound to study the structure-function relationship in supramolecular architectures which are commonly used in electronic materials design.

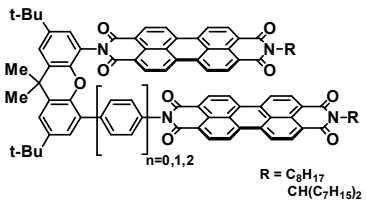

Figure 1. Investigated Molecules.

A series of covalently-bound cofacial PDI chromophores (Fig. 1) with varying degrees of electronic interaction were recently studied to interrogate the effect of *H*- and *J*-aggregation on optical and electronic properties. Using femtosecond transient absorption spectroscopy, the nanosecond formation of ^{3*}PDI or a PDI excimer-like state was observed that was dependent on the degree of electronic coupling, facilitated by the solvent polarity. By monitoring the C=C core stretching motions of PDI (1400-1600 cm^{-1}) with femtosecond stimulated Raman spectroscopy (FSRS), triplet formation in most cases was unexpectedly observed to occur via spin-orbit-induced charge transfer intersystem crossing (SOCT-ISC). SOCT-ISC requires a charge separated state between nearly orthogonal orbitals to produce strongly coupled radical ions that result in rapid formation of triplet states upon charge recombination.[1] In this case, the charge transfer (CT) state was observed to occur between PDI and the xanthene bridge, $PDI^{-\bullet}$-$Xan^{+\bullet}$ within 3 and 60 ps, depending on solvent polarity and electronic coupling. FSRS reveals that triplet formation is preceded by the characteristic frequency shift that indicates charge transfer from ^{1*}PDI to the $PDI^{-\bullet}$.[2] Significantly, the consistency in observed rate of charge recombination (1.1 – 1.5 ns) from $PDI^{-\bullet}$-$Xan^{+\bullet}$ to ^{3*}PDI, elucidated by FSRS, strongly suggests that SOCT-ISC is the predominant mechanism of triplet formation in this series of molecules.

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S_2 Fluorescence Dynamics of *meso*-Aryl-substituted Subporphyrins

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Porphyrins represent one of the most widely and intensively studied macrocyclic ring systems since these systems have been recognized as key pigments in photosynthesis. On the other hand, the photophysical behaviors of subporphyrins, which are one of well-known synthetic analogues of porphyrins, are little known. In addition, the S_2 fluorescence of subporphyrin has never been reported. Thus, the focus in the current investigation is whether the S_2-fluorescence of subporphyrins can be detected or not. It is also intriguing to determine the S_2 lifetimes of subporphyrins and to identify structural features that affect these lifetimes

Besides S_1 fluorescence, another fluorescence bands were observed for subporphyrins **1**-**4** upon excitation at the respective Soret-like band (Fig. 1). These fluorescence spectra have been assigned as S_2 fluorescence on the basis of their mirror images of the S_2-S_0 absorption. To explore the intrinsic excited state relaxation dynamics of **1**-**4**, fluorescence transients were recorded with our fluorescence up-conversion apparatus. Interestingly, we find that the S_2-S_1 IC rates of **1**-**4** are approximately five times faster than that of ZnTPP. Furthermore, despite different axial substituents such as methoxy, phenyl and naphthyl groups, the S_2-S_1 IC rates of **1**, **2**, and **4** are similar to each other. The p orbitals of B-axial substituent and the main π-system are orthogonally oriented. It seems to have no significant interaction between the central subporphyrin π-system and B-axial phenyl moiety. Hence we can expect that the S_2-S_1 IC rates of **1**, **2**, and **4** are almost identical in spite of different substituents.

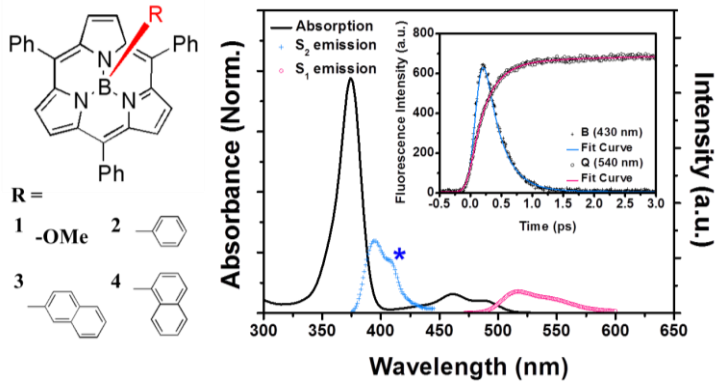

Fig. 1 Molecular Structure of Subporphyrins **1**, **2**, **3**, and **4**, and the ground-state absorption and static fluorescence spectra of **1** in toluene. (Inset: Time-resolved fluorescence decay profiles of **1**)

Ultrafast dynamics of solvent coordination to organometallic photoproducts probed via solvent vibrational oscillators

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In ultrafast spectroscopic studies on the photolysis of organometallic complexes, it is important to know the dynamics of solvent coordination to the vacant site of the photoproduct. Previous time-resolved spectroscopic studies have monitored the rise time of the vibrational bands of solvated photoproduct molecules upon solvent coordination to determine the timescale for this process. This approach carries implicit limitation of spectral broadening of hot vibration. To avoid this limitation, we have instead elected to probe coordination dynamics via solvent vibrational oscillators using time-resolved infrared(TRIR) spectroscopy.

We selected acetonitrile (AcCN) as target solvent, due to its high oscillator strength. Solvent coordination dynamics are determined by tracing a combination band at 2294 cm^{-1}, since this band disappears upon coordination of an AcCN molecule to the metal center (regardless of whether CH or CN coordinates). Among many photoproducts, such as $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $Fe(CO)_4$ and $Mn(CO)_5$, the coordination times are about 7-10 ps, which are about four times longer than reported values by previous studies [1,2]. We attribute this result to suggest that solvent coordination only occurs after vibrational and rotational excitations of the nascent photoproduct have cooled to (near) thermal equilibrium.

On the other hand, the 2254 cm^{-1} band of depleted AcCN molecules is strongly overlapped with ν_{CN} of photoproduct-coordinated AcCN molecules, preventing a quantitative kinetic trace. However, the redshift in frequency of photoproduct-coordinated AcCN does give a quantitative comparison of pi back-bonding electron donation in the various transition metals complexes studied.

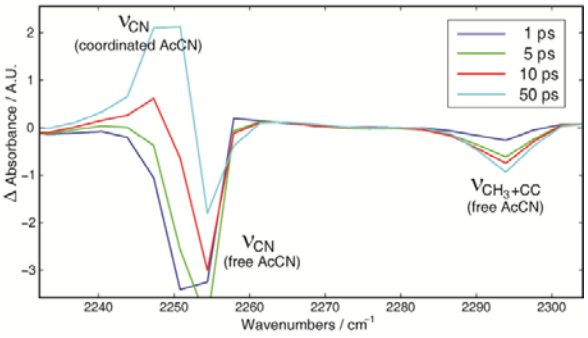

Fig.1. TRIR spectra of AcCN in AcCN solution of $W(CO)_6$ following 267 nm excitation

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Bimolecular Electron Transfer between Pyrene and 1,4-Dicyanobenzene as Studied by Nanosecond Time-Resolved Near/Mid-Infrared Spectroscopy

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Photoinduced bimolecular electron transfer (BET) reactions [1,2] are one of the fundamental photophysical processes that have significant importance in solar energy conversion and photosynthesis. Understanding the charge recombination (CR) process is very crucial for preventing charge loss during solar energy conversion. The dynamics of both cation and anion formed via BET, which is essential to understand the CR dynamics, can be unequivocally observed with time-resolved infrared spectroscopy compared with conventional transient absorption spectroscopy. Here, we study the CR dynamics between pyrene (Py) and 1,4-dicyanobenzene (DCB) as a model system for BET, using our near/mid-infrared (NIR/MIR) spectrometer [3]. A 7-ns laser pulse at 355 nm is used to excite the $S_1 \leftarrow S_0$ transition of Py in the presence of DCB, generating a pair of $Py^{\bullet+}$ and $DCB^{\bullet-}$. Subsequent CR dynamics is probed with either NIR or MIR light. Intense vibrational bands of $Py^{\bullet+}$ are observed at 1580, 1212 and 1136 cm^{-1} in the fingerprint region, corresponding to ring CC stretching modes, whereas a band observed at 2100 cm^{-1} corresponds to the CN stretch of $DCB^{\bullet-}$. In the NIR region, electronic bands of $Py^{\bullet+}$ are observed as well (lower panels of Fig. 1). Interestingly, we found a considerably different relaxation dynamics between the cation and the anion in acetonitrile solution (lower panels of Fig. 1), which is in apparent contradiction to the neutrality of the system. We interpret this discrepancy in the CR rates of the cation and the anion in terms of the role of acetonitrile in scavenging electron released by $Py^{\bullet+}$ in the solution and thereby providing an additional CR channel via solvent.

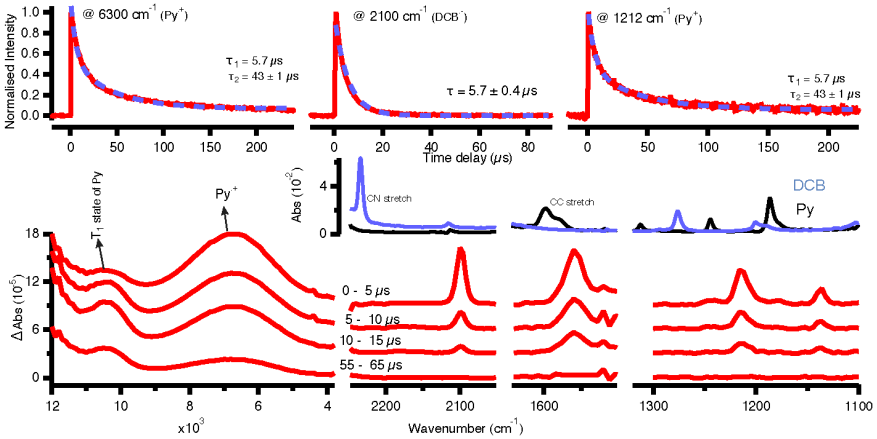

Fig. 1 Kinetic profiles (upper panels) and transient NIR/MIR spectra (lower panels) of $Py^{\bullet+}$ and $DCB^{\bullet-}$ and FTIR spectra of Py and DCB in acetonitrile solution (middle panels).

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Two-dimensional broadband mid-IR spectroscopy

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This study reports on the development of a 2D IR spectrometer in the pump-probe geometry utilizing a broadband mid-IR pulse as a probe field.

We have recently developed a source of broadband mid-IR pulses tunable from 2.5 – 8 μm with spectral bandwidth exceeding 2000 cm^{-1} by focusing 800 nm/400 nm femtosecond pulses into various gas media. The input 800 nm light is doubled to 400 nm in a type I BBO crystal. The two orthogonally polarized ω/2ω pulses encounter a birefringent calcite crystal for time delay compensation and are subsequently focused in various gas media (air, argon, neon and nitrogen) contained within a 1.2 m gas cell using a 1 m focal length silver mirror. The tunability of the broadband mid-IR pulses arises from using different gases, varying the pressure of a gas and the amount of incident 800 nm/400 nm light focused into the gas cell at a given pressure. Characterization of the mid-IR pulses shows that a four-wave mixing process plays a major role in broadband IR generation. We measure IR energies as high as 0.5 μJ/pulse for an input 800 nm energy of 3 mJ/pulse in 900 Torr of Argon. The intensity fluctuations of the mid IR pulses are ~2% for a 2-hour period. A temporal characterization of the broadband pulses using the X-FROG technique finds the pulse width to be sub-20 femtoseconds. We report on 2D IR studies of strongly H-bonded systems using this novel source in a 2D IR spectrometer.

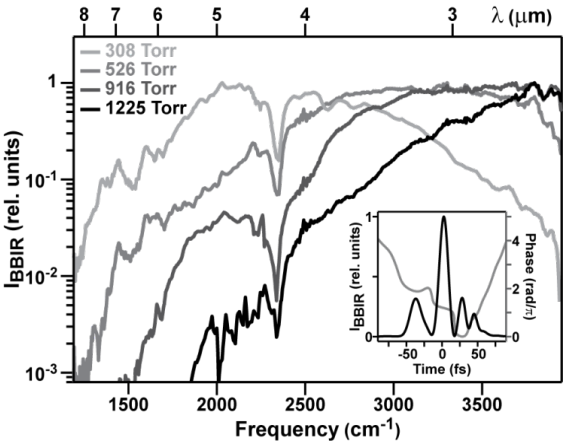

Figure 4. Broadband IR spectra as a function of pressure for air. The inset shows the reconstructed electric field intensity and phase of the IR pulse revealing a sub 2-cycle pulse centered at 2.5 μm.

References:

[1] M. Cheng, A. Reynolds, H. Widgren and M. Khalil, Opt. Lett. **37** (2012) 1787.

Femtosecond OPA pumped by 1030 nm Yb:KGW laser

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A widely used method for production of short pulses in the region 1-10 μm is based on the generation of signal and idler waves in a traveling–wave optical parametrical generator or an amplifier (OPA) pumped with a commercial femtosecond Ti:sapphire laser and subsequent difference frequency generation (DFG) between these two waves. Using longer pump wavelengths, such as 1030 nm delivered by Yb-doped potassium gadolinium tungstate (Yb:KGW) lasers, enables generation of short tunable pulses at 1.2 – 9 μm without a DFG unit.

We present a compact and simple mid-infrared OPA setup without DFG. Pumping with transform-limited pulses and using a home-built passive pulse-shaper enables generation of pulses of 160 fs length. A negatively chirped pump increases the output energy 1.5-2 times and makes possible the generation of nearly transform-limited pulses with 280-330 fs lengths.

Our set-up is based on a commercial Nd:KGW laser (Pharos, Light Conversion Ltd.) providing up to 1 mJ pulses of 200 fs pulse-length at a repetition rate of 2 kHz. We used pulse energies of 400 μJ to pump the OPA.

A white–light continuum is generated in a 2-mm sapphire window to seed the first amplification stage with a 5-mm ß-barium borate crystal. This stage is pumped at 515 nm by a second harmonic of the fundamental. The amplified seed is further amplified by a second and a third stage in a 2-mm-thick silver thiogallate crystal pumped with the fundamental pulse-energies of 27 μJ and 260 μJ, respectively.

The aim of pumping with negatively chirped pulses is to maximize the output energy of mid-infrared pulses. To generate shorter mid-infrared pulses, we pumped the OPA with the shortest 200 fs transform-limited pulses delivered by the Nd:KGW laser. As the OPA's output pulses are not transform-limited, we used a passive pulse-shaper consisting of two sapphire wedges movable relative to each other to compress mid-infrared pulses [1]. The passive pulse-shaper is alignment free and exhibits energy losses of about 10% to 30% in the spectral range of 2.6 μm to 4.6 μm.

References:

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Analyzing brominated Al-Corroles with Vis-pump and IR-, NIR- and VIS-probe experiments.

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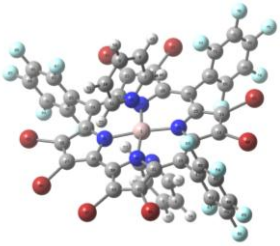

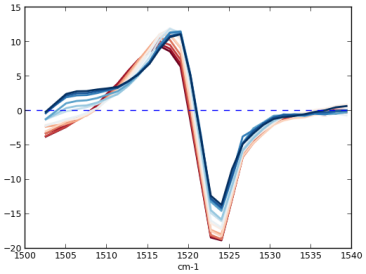

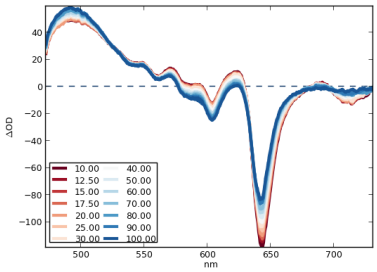

Corroles are an emerging class of photoactive molecules with remarkable chemical and photophysical properties and relatively unexplored potential. We investigated ultrafast dynamics of different Al-corroles using a combination of pump-probe experiments in different spectral ranges. Here we present the results of our studies on brominated Al-corroles $Br_8Al(tpfc)(py)_2$. In the infrared range (IR), we probed the v(C=C) marker band vibration at 1521cm^{-1}. In the visible (VIS), we used a white light continuum as probe (450 nm – 750 nm). Furthermore, measurements around 1000 nm in near infrared (NIR) were performed for probing the S_1 band -> Soret-band transitions. We excited the $Br_8Al(tpfc)(py)_2$ samples on the low energy side at 640 nm to reduce energy relaxation processes.

In the visible, the most striking feature is a decay of the simulated emission with a time constant of 95 ps, which is not observable for non-brominated Al-corroles. We attribute this to an intersystem crossing (ISC) due to the heavy atom effect of the bromine. In total, a four exponential model with time constants of 0.3ps, 1.6ps, 8.5ps and 95 ps is fitting the data well.

The NIR-data shows that the S_1 state is losing population with 95 ps, and additionally on a sub 10 ps time scale. The combination of time-resolved electronic and vibrational spectroscopy allows for an assignment of emerging vibrational bands in the triplet state, and intersystem crossing reaction channels in corrole molecules.

References:

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Initial interfacial structure and dynamics of dye sensitizer under photo-excitation studied by ultrafast infrared spectroscopy

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The dye-sensitized solar cell provides a technically and economically credible alternative concept to present day p-n junction photovoltaic devices. To understand such photo-energy conversion process in detail, however, information about the electronic structure and carrier dynamics at the semiconductor/dye interface becomes important. In this study, we applied femtosecond infrared absorption spectroscopy to characterize the photo-excited initial structure of dye sensitizer in solution and interfacial structure of TiO_2/dye interface.

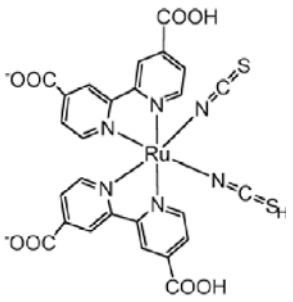

Figure 1. N719 dye

In this experiments, *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)bis(tetrabutylammonium) (N719) was used as a sensitizer as shown in Fig. 1. Transparent TiO_2 film were prepared from colloidal solution and deposited on the CaF_2 window. Femtosecond time-resolved visible-pump/IR-probe measurements were carried out by using Ti:sapphire regenerative multipath amplifier system, which was synchronously pumped by a mode-locked YLF laser. The IR probe pulse (2.5-6.0 μm, bandwidth 200 cm^{-1}, 0.1-0.8 $mJpulse^{-1}$) and the visible pump pulse (395 nm and 540 nm 0.5-9.0 $mJpulse^{-1}$) were generated by using an optical parametric amplification/optical parametric generation (OPA/OPG) and differential frequency generation (DFG) system. IR probe beam was split into two beams as "signal" and "reference" on to the sample and then detected with a monochromator, which was coupled with a liquid nitrogen-cooled 64x2 element MCT double linear array system [1].

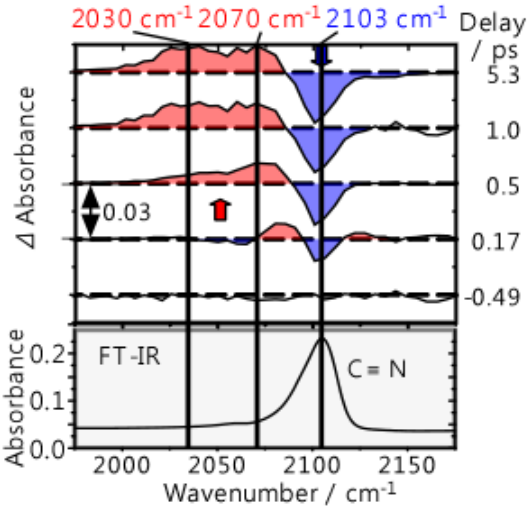

Figure 2. Transient absorption spectrum of N719 in acetonitrile solution.

Figure 2 shows the NCS stretching region of transient absorption IR spectra of N719 in acetonitrile solution after MLCT excitation by 540 nm pump pulse. A decrease of Δabsorbance centered around 2103 cm^{-1} was observed and a broad transient absorption peak centered around 2030-2070 cm^{-1} emerged. The negative band appeared at 2103 cm^{-1} was assigned to the decrease of S0 state and positive band appeared around 2030-2070 cm^{-1} to the appearance of T1 state, respectively. The difference in the ultrafast dynamics between homogeneous (in solution) and heterogeneous (on TiO_2 surface) systems were also discussed.

Reference

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Elucidating the mechanism of a unidirectional molecular motor

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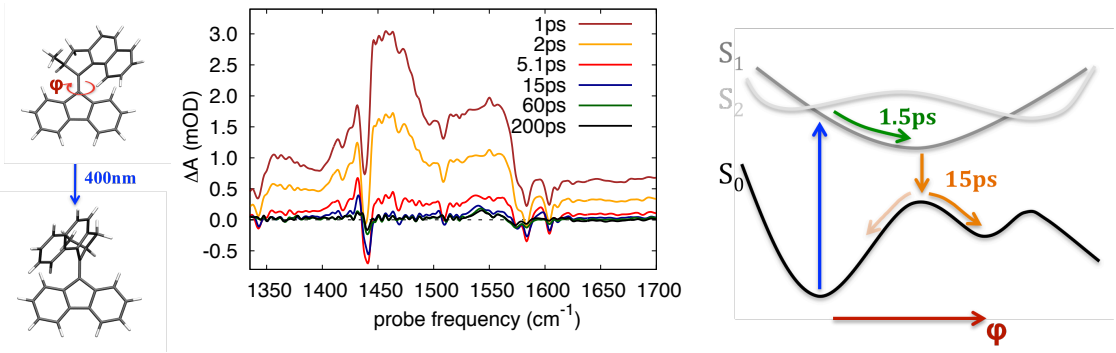
One of the major challenges in developing artificial molecular machines is to obtain control over the directionality of the motion. Based on chiral overcrowded alkenes, it is possible to synthesize molecular motors which perform unidirectional rotation through consecutive photochemical and thermal steps. In order to understand the operation mechanism of these motors, structure-sensitive spectroscopic measurements with high time-resolution are essential. Recently, time-resolved fluorescence and UV/Vis transient-absorption studies have provided a first glance on the photochemical step of the operation cycle. [1]



Here, we present UV-pump/IR-probe experiments in combination with *ab-initio* calculations, which allow us to follow the structural evolution of the molecular motor in detail. We find that two close-lying electronically excited states are involved in the structural rearrangement, giving rise to a broad IR electronic absorption band combined with narrow vibrational bands. By fitting the data to a two-step kinetic model, a time constant of 1.5±0.5ps for the first step of the rotation cycle is obtained. The subsequent steps, which involve electronic relaxation to the ground state and a cooling process, take place on a time scale of 15±5ps. The delay dependence of the anisotropy reveals additional details of the motor movement.

Reference:

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Towards excited-state surface-enhanced femtosecond stimulated Raman spectroscopy

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As interest in plasmonic photovoltaic and catalytic systems grows it becomes increasingly important to investigate how metal surfaces affect ultrafast dynamics and electron transfer. However, to understand the mechanistic details of these processes we must probe reaction dynamics on the appropriate temporal and spatial scales: the femtosecond timescale of nuclear motion and the sub-nanometer length scale of atoms. Towards this end, we developed a new technique called surface-enhanced femtosecond stimulated Raman spectroscopy (SE-FSRS)[1] which combines the high plasmonic enhancements of surface-enhanced Raman spectroscopy (SERS) with the high spectral and temporal resolution of femtosecond stimulated Raman spectroscopy (FSRS). While recent studies have explored the affects of substrate particle size on the observed fano-like resonances of SE-FSRS,[2] a number of questions remain about appropriate substrate systems to optimize SE-FSRS signals.

This work explores different substrate systems for use in SE-FSRS. We have investigated a range of plasmonic substrates with and without a silica protective layer in order to understand how best to apply SE-FSRS for excited-state studies. These results provide insight into the damage mechanisms previously observed in SE-FSRS and also provide more accurate approximations of the enhancement factor for this technique.

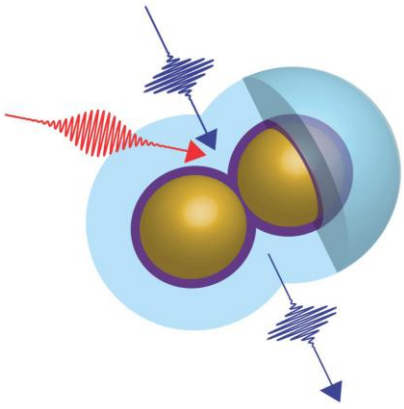

Fig 1. Silica-coated gold nanoparticle dimers have been demonstrated to be a successful SE-FSRS substrate system.

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(1) Frontiera, R. R.; Henry, A. I.; Gruenke, N. L.; Van Duyne, R. P. *J Phys Chem Lett* **2011**, *2*, 1199.
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Folding of a light-switched β-hairpin peptide: Comparison of isomerization and temperature-jump induced peptide dynamics.

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A number of different techniques are used to follow the most rapid processes in peptide folding. Among them one finds rapid mixing, pressure- or temperature-jump (T-jump) experiments. In these experiments structural changes of the peptides are initiated indirectly by a fast change in the environment. Recently another approach was introduced where the isomerization reaction of a back-bone element was used to initiate ultrafast structural changes. In these light-triggered peptides the structural changes are induced by an intrinsic part of the peptide. Although both approaches have been used extensively to study folding or unfolding reactions of different peptides the direct connection between the dynamics observed with one method with the observations from the other is difficult to establish. Qualitatively one might expect the isomerization induced peptide dynamics to be a force-driven process that is much faster than the dynamics initiated by a change in temperature. However a detailed comparison of the methods is still missing.

In this work we apply T-jump and light-triggering to investigate structural changes of a light switchable β-hairpin. The model peptide consists of two amino acid strands connected by an azobenzene switch. When the azobenzene is in the *cis* conformation the peptides form an ensemble containing a large fraction of folded β-structures. When azobenzene is in the *trans* conformation no folded hairpin structure is observed [1].
In the first set of experiments the folding of the peptide was initiated by an ultra short UV light pulse inducing the *trans – cis* isomerization of azobenzene and leading to the formation of the *cis* ensemble. The structural changes are observed via time resolved probing in the mid-IR. After rapid transients related with the isomerization of the azobenzene switch and the rearrangement of its surroundings on the 1 ns time scale [2, 3] we observe reaction dynamics on the time scale of 10 to 100 μs showing strong temperature dependence. T-Jump experiments are performed on the same peptides in the *cis* ensemble. Here the temperature jump, induced by a near infrared laser pulse, changes the ratio of folded/unfolded structures and the relaxation into the new equilibrium is studied by IR- spectroscopy. The comparison of the results obtained with the two methods leads to an improved understanding of the induced processes and allows us to obtain a detailed model for the folding of the β-hairpin peptide.

References:

[1] S.-L Dong, A photocontrolled beta-hairpin peptide. Chem.Eur.J. 12, 1114-1120 (2006)
[2] T.E. Schrader, Folding and unfolding of Light-triggered beta-hairpin model peptides. J.Phys.Chem.B 115, 5219-5226 (2011)
[3] T.E. Schrader, Light-triggered beta-hairpin folding and unfolding. PNAS 104, 15729-15734 (2007)

Links between Structure, Dynamics and Function in the Inhibition of Catalase by Nitric Oxide

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This study investigates the *Corynebacterium glutamicum* catalase enzyme from a variety of perspectives including in vitro biochemistry and whole organism biology through to atomistic level protein structure and ultrafast dynamics in order to examine directly the link between structure, dynamics and function. We confirm biochemically that the binding of nitric oxide (NO) at the haem-centre leads to inhibition of catalase function, which is the conversion of hydrogen peroxide into water and oxygen, while X-ray crystallographic data reveals that the active site structure includes the presence of a chain of hydrogen-bonded water molecules that interact directly with the NO ligand. Correlation of this data with ultrafast two-dimensional infrared spectroscopy indicates that this water-protein interaction results in a dynamically-restricted haem-binding site and suggests a molecular basis for both the inhibition of biological activity and the governing role that structural water plays in catalase function.

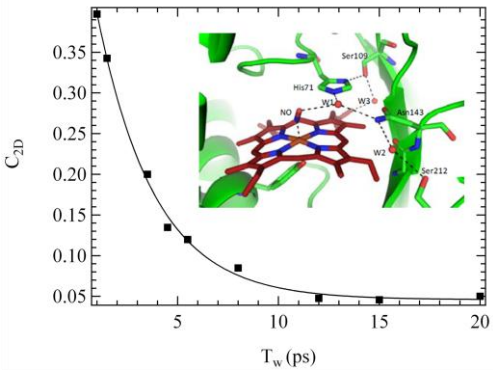

Fig. 1 Spectral diffusion dynamics of the nitrosylated catalase with, inset, the crystal structure of its haem binding site.

Secondary and quaternary structural imaging of human hairs by using VSFG-detected IR super-resolution microscope

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We have developed vibrational sum-frequency generation (VSFG) detected IR super-resolution microscope with a sub-micrometer spatial resolution until now, and have reported the applications to various biological samples including living cells [1, 2]. In this study, we applied an IR super-resolution microscope to human hairs.

Human hair is a complex biological material consisting of distinct morphological components and is well-known to compose of the medulla, cortex, and cuticle regions from inside to outside. At the cortex area occupying 90% of human hair, keratin protein, which is primary component of human hair, forms a line in the shape of fiber along the longitudinal direction of human hair, and controls physical properties such as flexibility, strength, softness and curliness. To understand the relationship between physical properties and the internal nanostructure, we attempted IR imaging at IR super-resolution in the 6-9 μm mid-IR region.

As a result, we succeeded in obtaining VSFG image in the amide III band at 1250 cm^{-1} with sub-micrometer spatial resolution, and clearly observed strong VSFG signals only from the cortex area (see Figure 1). VSFG image seems to be contributed to the IR mapping of the distribution of α-helix structure at the cortex. This is supported by very weak emission from the cuticle and medulla, those do not have an α-helix structure.

In the presentation, the internal nanostructure, that is, quaternary structure of human hairs will be also discussed in detail.

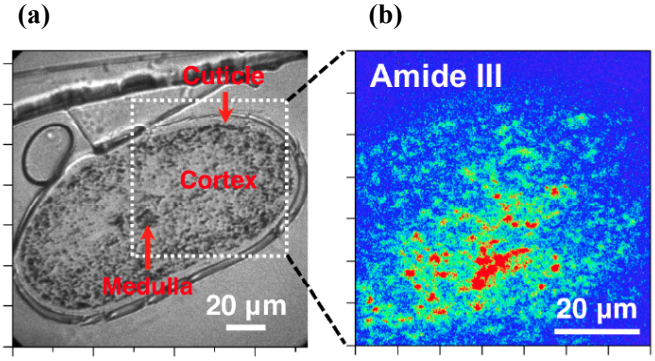

Fig. 1. (a) Transmission image of the cross section of a human hair. (b) VSFG Image obtained by the simultaneous introduction of visible and IR beams (ν_{VIS} = 610 nm, ν_{IR} = 8000 nm (1250 cm^{-1})).

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[1] K. Inoue, M. Fujii, M. Sakai, Appl. Spectrosc. **64** (2010) 275.
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Dynamics of two-photon isomerization of DTTCI observed by femtosecond pump-probe and two-pulse correlation measurements

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Unimolecular reactions, such as photoisomerization, are important to understand the elementary steps of chemical reactions, and substantial effort has been dedicated to reveal the reaction mechanisms. Photochemical reactions initiated by multiphoton absorption are essentially different from conventional photochemical reactions because the character of the populated state depends on the optical order of the excitation process and new photochemical reaction channels are opened through the excitation of reaction intermediates. In this regard, knowledge of the contribution of the multiphoton process to photochemical reactions is necessary to exploit new photochemical reaction pathways [1], and the multiphoton process is expected to play a vital role in the optical control of chemical reactions.

In this study, we examined the multiphoton-induced reactions of DTTCI (3,3'-diethyl-2,2'-thiatricarbocyanine iodide), such as photoisomerization and/or photodegradation by red-tail excitation, using a femtosecond near-infrared (NIR) pulse. Pump-probe transient measurements revealed that the isomers and the leuco forms were generated through the two-photon process and the reaction time for the photoisomerization was 0.5 ns as shown in figure 1. The photoisomerization process was investigated by two-pulse correlation (2PC) measurements [2], in which the sample was excited by two pump pulses and the pump-induced transient absorption change was monitored by a probe pulse as a function of the interval between the two pump pulses. It was found from 2PC measurements that the excitation process from S_0 to S_n states involved a two-step excitation in parallel with two-photon absorption. The double exponential decay behavior was observed in the 2PC trace and assigned to IVR (τ ~ 0.1 ps) and vibrational relaxation (τ ~ 5 ps) processes in the S_1 state in the two-step excitation process.

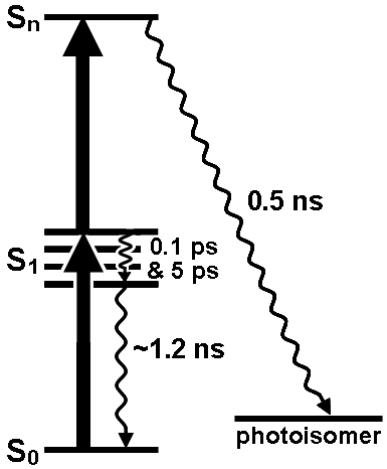

Fig. 1 Schematic diagram of two photon isomerization dynamics.

References:

[1] M. Fuyuki, et al., Journal of Photochemistry and Photobiology A : Chemistry, **252** (2013) **152**: Chem. Phys. Lett., **511** (2011) 45: Chem. Phys. Lett., 499 (2010) 121.
[2] K. Furuta, M. Fuyuki, A. Wada, Appl. Spectrosc., **66** (2012) 1475.

Ultrafast hydrogen-bonding dynamics in the electronic excited state of photoactive yellow protein

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The ultrafast structural dynamics in the electronic excited state of photoactive yellow protein (PYP) is studied by femtosecond stimulated Raman spectroscopy. Stimulated Raman spectra in the electronic excited state, S_1, can be obtained by using a Raman pump pulse in resonance with the S_1-S_0 transition. This is confirmed by comparing the experimental results with numerical calculations based on the density matrix treatment. This method enables us to discuss the stimulated Raman spectra in the S_1 state without knowledge of the S_2 state potential [1].

We also investigate the hydrogen-bonding network surrounding the wild-type (WT)-PYP chromophore in the ground and excited states by comparing its stimulated Raman spectra with those of the PYP mutants as shown in Fig. 1. We focus on the relative intensity of the Raman band at 1555 cm^{-1}, which includes both vinyl bond C=C stretching and ring vibrations and is sensitive to the hydrogen-bonding network around the phenolic oxygen of the chromophore. The relative intensity for the WT-PYP decreases after actinic excitation within the 150 fs time resolution and reaches a constant intensity. These observations indicate that the WT-PYP hydrogen-bonding network is immediately rearranged in the electronic excited state after actinic excitation.

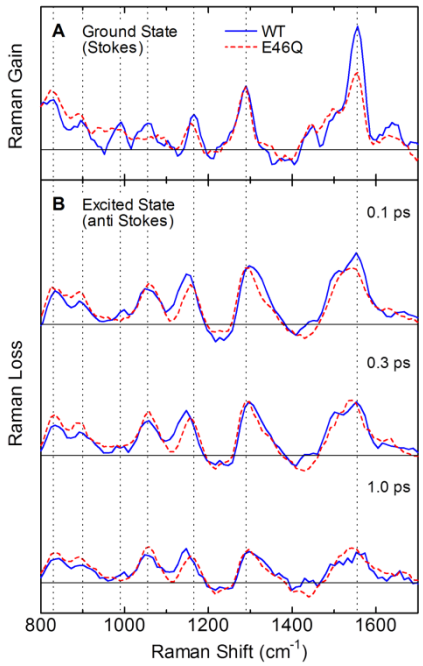

Fig. 1 Stimulated Raman spectra of WT-PYP (solid line) and E46Q-PYP (broken line) measured at the ground state (A), and measured at 0.1, 0.3, and 1.0 ps after actinic excitation (B). Raman pump energy is 19214 cm^{-1}.

References:

[1] R. Nakamura et al., J. Phys. Chem. B **116** (2012) 14768.

Time-resolved IR spectroscopy of hydrogenase enzyme mimics: the effect of hydrogel encapsulation

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Synthetic model compounds of the active site of the hydrogenase (H_2-ase) enzyme have attracted much scientific attention as a result of their ability to catalyse the reversible reduction of protons to form dihydrogen. To address problems relating to air sensitivity and low conversion rate of these species, we have incorporated hydrogenase model compounds into low molecular weight (LMW), peptide based hydrogels. LMW hydrogelators are low-cost, biocompatible and highly tuneable materials with great potential for encapsulating enzymes with retention, or even improvement of catalytic activity.[1] Here, TRIR spectroscopy data for an H_2-ase mimic in a Fmoc-dileucine environment[2] are compared with those in various solvents in order to evaluate the influence of the environment on photochemistry and to shed light on the location of the mimic within the supramolecular structure of the gel.[3]

Results from the gel are consistent with an immobile hydrogen bonding environment that restricts dynamic processes such as photo-induced isomerisation while maintaining the fast (<100 ps) vibrational relaxation rates observed in solution, confirming the gel's unique properties. Further, evidence for prolonged existence (> 1 ns) of unsaturated diiron centers was observed after UV excitation suggesting stabilisation of these reactive intermediates.

Preliminary work on incorporation of a photosensitizer and electron/proton donors shows promising results regarding achieving the full H_2 catalytic cycle in this system.

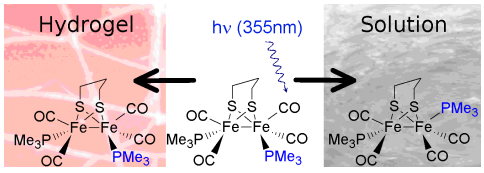

Fig. 1 Reduced photo-induced isomerisation of the hydrogenase mimic in the gel compared to solution.

References:

[1] Gao, Y.; Zhao, F.; Wang, Q.; Zhang, Y.; Xu, B. *Chem. Soc. Rev.* **2010**, *39*, 3425–3433.

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Real-time observation of destruction of hydration shells

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Interaction among substances including hydrophobic and hydrophilic interaction are governed by the structure change of water layers among them. Therefore, observation of structural change of hydration shells during a close contact among hydrated substances are important to understand many processes that take place in solutions. Here we have enabled a time-resolved IR absorption measurement by controlling a force between hydrated solutes by using electrochemical systems. [1,2]. Destruction process of hydration shell around tetrapropylammonium cation (Pr_4N^+) during a close contact on CO-covered Pt electrode was studied by time-resolved IR absorption spectroscopy.

First, we observed the change of CO by the electrode potential jumped from -100 to -800 mV. As shown in Fig. 1a, the peak top intensity at 2070 cm^{-1} was decreased within 10 ms. This change is due to the frequency shift of CO caused by the so-called “Stark tuning effect”. The time-constant of the frequency shift was identical with that of double-layer charging, suggesting that the electric double layer is reconstructed within 10 ms. Next, the change of water band was examined. By the negative potential jump, the band intensity at 3500 cm^{-1} increased in intensity within 10 ms (Fig. 1b). The band at 3500 cm^{-1} is ascribed to the water molecules of the hydration shell around Pr_4N^+ [1,2]. Therefore its increase suggests that the number of Pr_4N^+ at the interface increases. The time constants for the change of CO vibration and the increase of the concentration of Pr_4N^+ are the same. However, this band intensity starts to decrease after 20 ms (Fig. 1b), suggesting the destruction of hydration shell around Pr_4N^+. During the destruction of the shell, the band intensity at 3670 cm^{-1}, which is ascribed to the “free OH” on CO-covered hydrophobic surface, also decreased due to the removal of water on CO (Fig. 1c). Potential and temperature dependence of these rates were also examined.

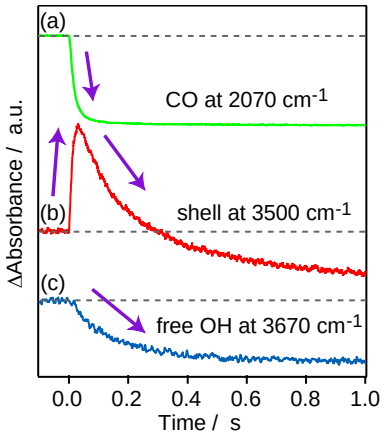

Fig. 1 Time-resolved IR absorption of the CO-covered Pt electrode by the potential jump from -100 to -800 mV vs Ag/AgCl. The bands of CO (2070 cm^{-1}), hydration shell around Pr_4N^+ (3500 cm^{-1}), and free OH on CO (3670 cm^{-1}) were measured.

References:

[1] A. Yamakata, M. Osawa, ***J. Am. Chem. Soc.* 131,** 6892 (2009).

[2] A. Yamakata, M. Osawa, ***J. Phys. Chem. Lett.* 1**, 1487 (2010).

Time-resolved FTIR study of a light-driven sodium pump rhodopsin

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An infrared spectrum provides molecular information about the vibrational modes, the types of transitions, and the transition probability. FTIR equipped with a step-scan mode can elicit excellently both spectral and temporal information in monitoring a rapid chemical phenomenon. The absorbance changes can be monitored with time resolutions down to nanoseconds and followed for time periods ranging over nine orders of magnitude. This technique is suitable for many proteins, including membrane proteins such as a light-driven proton pump bacteriorhodopsin [1-3].

Krokinobacter Rhodopsin 2 (KR2) is a microbial rhodopsin found in marine bacteria. Recent light-driven transport measurements revealed that KR2 belongs to a completely new functional class, a light-driven sodium ion pump [4]. Discovery of a new rhodopsin function motivated us to apply time-resolved step-scan FTIR spectroscopy to KR2, and we present time-resolved difference FTIR spectra of KR2 reconstituted into lipids (DOPC). According to flash photolysis, the primary K intermediate decays to a mixture of L and M intermediates, and finally O intermediate appears. Time-resolved FTIR spectroscopy monitors vibrational signals of these intermediate states, and structural dynamics during light-driven sodium ion transport will be presented.

References:

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[2] F. Garczarek and K. Gerwert, Nature 439, 109 (2006).
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Towards time-domain ultrafast vibrational spectroscopy of chemical reaction dynamics

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The advancement in ultrafast laser technology has made it possible to record vibrational spectra in the time domain over the full vibrational manifold. A long standing goal is to use time-domain based Raman spectroscopy to record vibrational spectra of excited electronic states. One of the major challenges is the decomposition of the recorded spectra into ground and excited state contributions. This has led to some controversy if it is at all possible to excite and detect high frequency vibrational coherences on excited states. Isolating the pure excited state coherence would enable one to follow chemical reaction dynamics with the ultimate temporal and spatial resolution.

Here we describe a new approach towards impulsive vibrational spectroscopy (IVS) that allows one to obtain excited state-only vibrational spectra. We demonstrate the capabilities of broadband-IVS by employing a three pulse scheme (ps-pump, fs -pump, probe) to measure the vibrational spectrum of beta-carotene in its first excited electronic state with high spectral resolution (<10 cm^{-1}). We also discuss preliminary results on an extension of this technique that allowed us to ultimately proof that it is possible to directly excite and detect high frequency (1800 cm^{-1}) coherences on excited states in a standard two-pulse transient absorption experiment. By employing broadband-IVS we are able to show that the strongly forbidden and previously unreported S_0-S_1 transition in beta-carotene does take place, albeit at a probability too small to be detected by electronic spectroscopy. Our results demonstrate the feasibility of performing time-domain vibrational spectroscopy with high-sensitivity purely based on electronic resonances decoupling the observation of vibrational structural dynamics from the necessity of large infrared or Raman scattering cross sections.

Bimodal dynamics of DNA bubbles

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DNA bubbles are thermal fluctuations in which the hydrogen bonds between the base pairs in a double-stranded DNA helix break, and the two strands become spatially separated. The formation of a DNA bubble plays an important role in DNA replication and gene expression via RNA transcription. Proton exchange NMR measurements have previously shown [1] that at body temperatures the bubble opening rate is much slower (milliseconds) than the closing rate (nanoseconds).

Here we investigate the bubble dynamics with transient infrared spectroscopy, whereby a perturbation to the equilibrium of the system is induced via a small (3-5°C) laser-induced temperature jump. By following the relaxation of the system to the new equilibrium using an IR probe pulse, the dynamics can be observed for a broad range of frequencies on a single-shot basis with a high time-resolution.

Homopolymers of poly(dA).poly(dT) and poly(dG).poly(dC) double-stranded helices have been investigated, along with their single-stranded counterparts. In contrast to ss-DNA, the transient spectra of the ds-DNA samples are composed of two spectral components with differing rate constants, implying that DNA bubble dynamics is not a simple two-state process, but one where the hydrogen-bonding and stacking occur on different time scales.

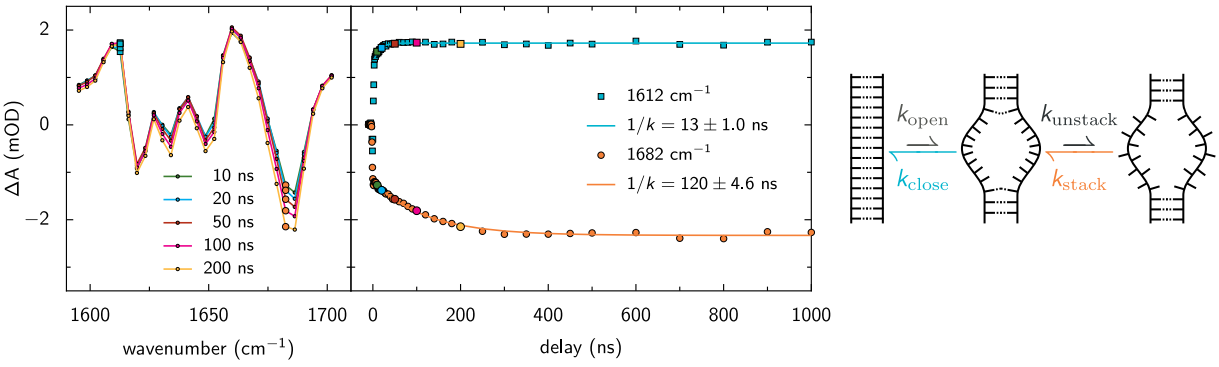

Fig. 1 DNA bubble dynamics probed by temperature-jump transient IR spectroscopy.

References:

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Determination of Huang-Rhys factors of multi-dimensional hyper-potential surfaces obtained by a few-cycle pulse laser

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Real-time vibrational spectra in poly[o-TFMPA([o-(trifluoromethyl)phenyl]acetylene)] (PTTPA) were observed using a 6.3-fs laser. Ultrafast geometrical relaxation from free excitons to self-trapped excitons (STEs) taking place around 20±2 fs was observed in PTTPA, and the thermalization time of 320±50 fs for STEs was determined.[1-2] As shown in Fig. 1(a), clear blue shift has been observed, which is due to the intra-chain thermalization process in which vibrational quanta of modes with high vibrational frequency are scattered to be converted low frequency modes via vibrational mode coupling. Six most intense vibrational modes with frequencies of 103, 171, 258, 377, 1201, and 1499 cm^{-1} can be observed in the FFT spectrum (Fig.1 (b)). Their vibrational dephasing time were calculated to be 694, 704, 840, 388, 733, 313 fs, respectively. And their Huang Rhys factors were calculated to be 0.224, 0.302, 0.179, 0.137, 0.0188, 0.0188, respectively. This is the first determination of multi-dimensional Huang-Rhys factors.

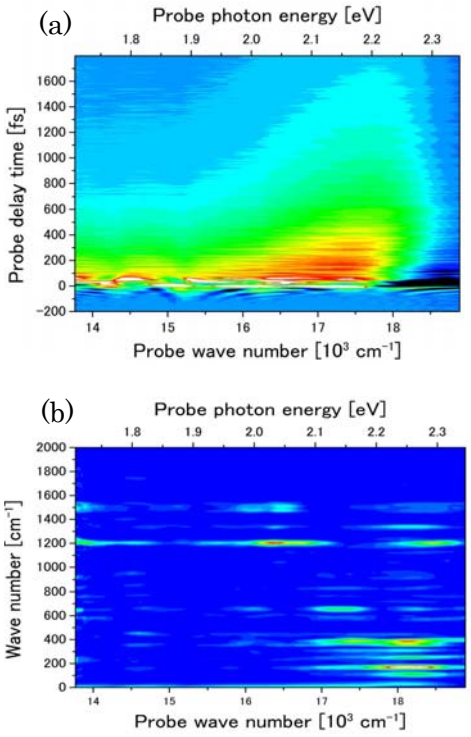

Fig. 1 (a) The two dimensional difference absorption spectrum. (b) The two-dimensional spectrum of FFT power.

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Ultrafast time-resolved pump/IR probe spectroscopy of [FeFe]-hydrogenase model compounds

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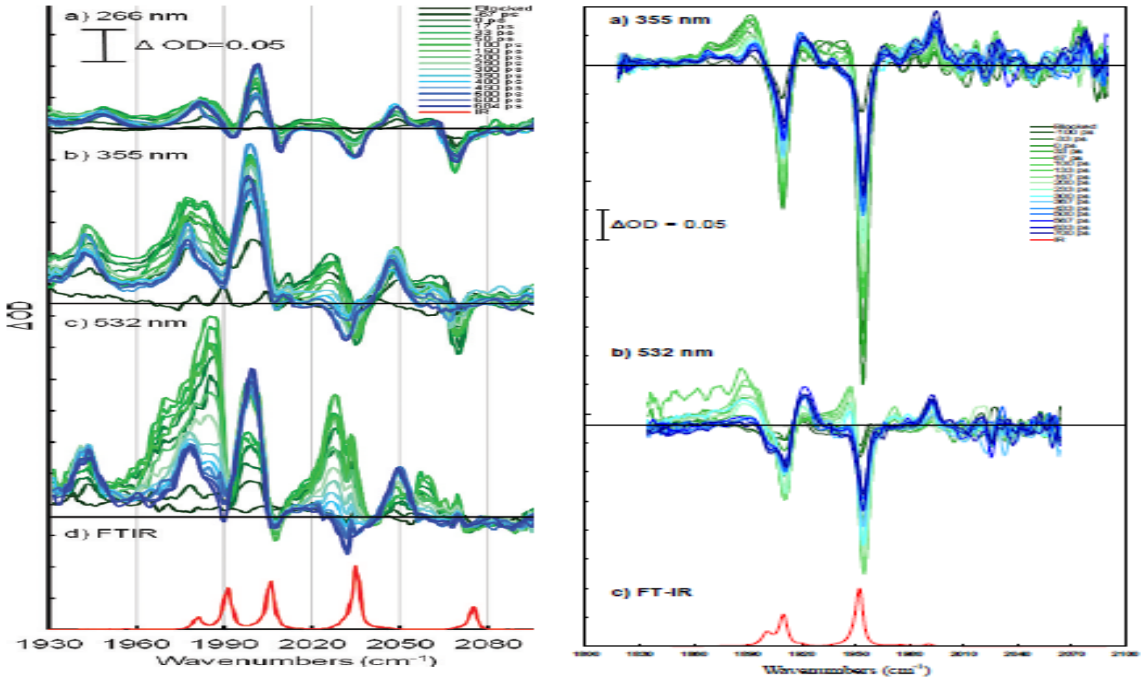
Time-dependent pump infrared probe studies of the [FeFe]-hydrogenase model compound $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(PMe_3)_2$ (PMe_3 = trimethylphosphine) in both acetonitrile and hexane solutions with pump wavelengths of 266 nm, 355 nm and 532 nm are presented. Previous work on $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ revealed two photoproducts generated upon UV or visible excitation, one involving the loss of a carbonyl, the other yielding a long-lived excited state with a lengthened Fe-Fe bond, depending on the excitation wavelength (left Fig) [1]. While a CO-loss product was observed, the long-lived excited state was not seen in the subject model compound although a third photoproduct involving isomerization of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(PMe_3)_2$ appears to be created. The same general excitation wavelength-dependence for $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ is also observed in the PMe_3 derivative, but is less pronounced (right Fig) [2]. By better understanding these hydrogenase model compounds, we gain valuable information for improving the light-driven (Photosynthesis II-like) catalysis for producing hydrogen using these and related synthetic compounds.



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PA41

Spectral diffusion of heavy water in presence of bromide and iodide ions at supercritical conditions: First principle molecular dynamics study

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The vibrational spectral diffusion and hydrogen bond dynamics of water molecules in presence of halide ions have been thoroughly investigated by *ab initio* molecular dynamics without employing any empirical potentials. We have run simulations at two different densities and two different concentrations of aqueous ionic systems. The time dependent trajectories are generated by using Car Parrinello[1] molecular dynamics and frequency calculation is done by time series analysis of wavelet method[2]. The underlying dynamics of vibrational spectral diffusion of water molecules inside and outside the solvation shell of ions have been investigated by computing hydrogen bond, dangling bond, rotational dynamics and frequency structure correlations of water molecules. We have found that the stretch frequencies of water molecules inside the solvation shell of ions are lower than those in bulk water molecules at supercritical condition. The results have been compared with experimental [3,4] and theoretical[5,6,7] data wherever available.

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Anomalous Blinking Characteristics in Single Molecule Surface-Enhanced Raman Spectroscopy (SMSERS)

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Light intermittency or 'Blinking' is a universal phenomenon in isolated quantum emitters such as single molecule and single quantum dot exhibiting bright and dark states with strong spectral fluctuations in time series. Of particular interest, asynchronous blinking behavior between different Raman bands with strong fluorescence background was observed in single molecule surface enhanced resonance Raman scattering (SMSERRS) [1]. In contrast to previous results, we observe synchronous blinking under nearly background-free conditions by quenching the fluorescence of Rhodamine 6G (R6G) dye molecules with silver nanoparticles, as shown in Fig. 1.

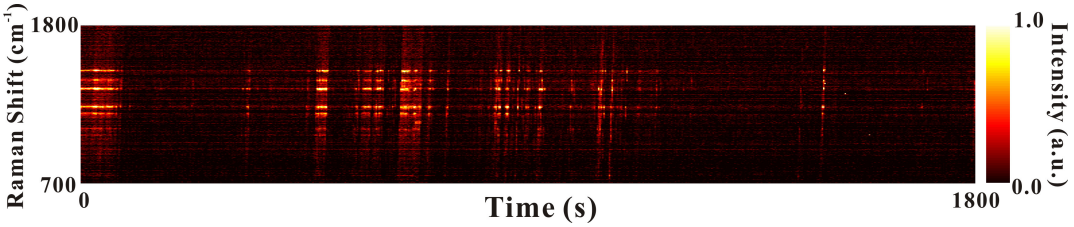

Fig. 1 SERS spectrum of a single R6G molecule adsorbed on silver nanoparticles.

By correlation analysis, we discovered a strong spectral correlation between functional groups of C-H off-plane bend, C-H in-plane bend, and C-C stretch in the aromatic ring. As shown in Fig. 2, the correlation coefficient between the abovementioned functional groups are all higher than 0.7. On the contrary, the spectral correlations between various functional groups and the background fluorescence are nearly zero. The synchronous blinking was attributed to the movement of R6G molecule in-and-out of the hot site.

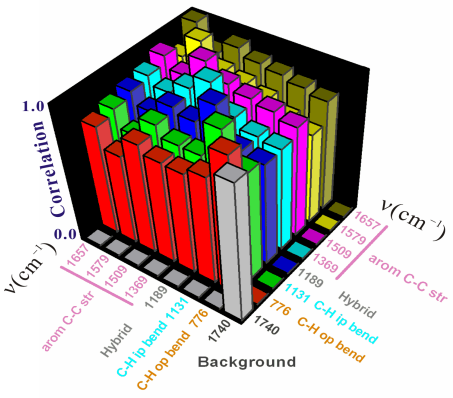

Fig. 2. Spectral correlation between various Raman bands.

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Intermolecular vibrational energy transfer analyzed by ultrafast two-dimensional infrared spectroscopy

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In the past, we have worked on the theoretical treatment of four-wave-mixing photon-echo spectroscopy as a tool to investigate the kinetic properties of molecular vibration systems[1,2]. In our approach, the photon-matter interaction is treated in the perturbative way which is standard in nonlinear and coherent vibration spectroscopy, while the couplings of the vibration mode with the environment or with other modes were treated non-perturbatively whenever possible. Analytical expressions of the spectral signals are also retained as much as possible. The direct extension of the application of this theory is to calculate the two-dimensional infrared spectra of the systems. In the present work, we analyze an intermolecular energy transfer process using two-dimensional infrared spectroscopy, as observed for instance by Bian et al. [3]. The time dependence of the cross-peak amplitude revealing the intermolecular energy transfer is evaluated from our analytical description which enables a detailed discussion of the role played by various internal processes acting on the individual donor and acceptor molecules participating in the energy transfer. Even if temperature effects are included in the description, for the present purpose, they do not play an important role due to the particular situation of large bandwidths of the laser pulses and the near-resonant vibrational modes involved in the process.

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Poster Presentation Tuesday

PB1

Anharmonic and solvent effects on Franck-Condon factors with application to molecular electronic spectroscopy

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Franck-Condon factors bridge the gap between theoretical modeling and experimental observations for molecular electronic spectroscopy and electron transfer. Under the displaced harmonic oscillator approximation, multidimensional Franck-Condon factors are decomposed into a product of many one-dimensional (1D) Franck-Condon (FC) factors, and each 1D-FC factor is associated with one Huang–Rhys factor that determines the leading contribution of band shape and intensity of corresponding normal-mode vibronic spectrum. Duschinsky rotation effect and anharmonic effect can be introduced into FC factors to further improve simulation in gaseous phase. However, strong interaction between solute and solvent results in direct modification of the leading term contribution, namely Huang–Rhys factor for each normal mode. The other minor effects (Duschinsky rotation and anharmonic) are mostly washed out by inhomogeneous broadening in solution.

We recently developed analytical formulas of anharmonic correction in FC factors in terms of Huang–Rhys factors for modeling absorption and fluorescence spectra in gaseous phase [1]. The analytical formulas were successfully applied to simulate absorption and fluorescence spectra for pyridine, fluorobenzene, and pyrimidine molecules and its results agree well with experimental observations [2-4]. On the other hand, we developed the scaling method leading to direct modification of Huang–Rhys factors for modeling absorption and fluorescence spectra in solution phase and this method was applied to perylene molecule in benzene solution [5].

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Ultrafast isomerization dynamics of a substituted azobenzene driving a cyclodextrin shuttle

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Growing interest in performing molecular-scale mechanical work has led to an increase in the synthesis of complex supramolecules capable of undergoing controllable, unidirectional structural changes. Better understanding of how the small-amplitude, ultrafast, molecular motions within these materials are connected to larger-scale processes may lead to improved material designs. However, the motions of many supramolecular systems involve non-chromophoric components, which are difficult to examine spectroscopically. A previously reported rotaxane [1], in which shuttling of the cyclodextrin host is initiated by isomerization of a substituted azobenzene guest (Fig. 1), is well-suited to spectroscopic investigation, because the process can be photoinitiated, and because the shuttling motion is closely associated with the photoisomerization of the spectroscopically active azobenzene moiety.

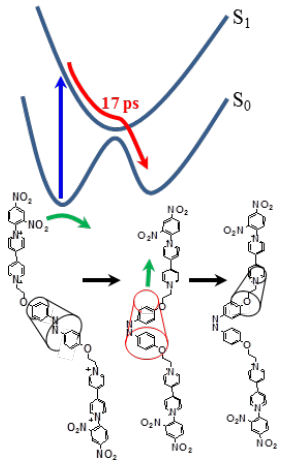

Fig. 1. Isomerization scheme for rotaxane.

We synthesized the rotaxane according to the literature procedure [1] and monitored its excited state dynamics using time-resolved spectroscopy. Since relaxation of photo-excited azobenzene-based molecules from the S_1-excited state precedes isomerization [2], we used this data to analyze the effects of the cyclodextrin host on the rotaxane isomerization. The time constant for excited state relaxation of the rotaxane is *ca.* 17 ps, whereas that of the guest molecule without the cyclodextrin host is *ca.* 5 ps. The reduction in the isomerization rate of the rotaxane relative to the isolated guest molecule confirms that the isomerization process is sterically inhibited by the host. Successful isomerization in the constrained environment then creates a steric repulsion that drives the cyclodextrin off of the azobenzene moiety.

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PB3

Femtosecond stimulated Raman spectroscopy of a BLUF protein PapB from the purple bacterium *Rhodopseudomonas palustris*

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BLUF (Blue Light sensing Using FAD) protein is a blue light receptor which utilizes FAD (flavin adenine dinucleotide) as the chromophore. When a BLUF protein catches blue light, the protein turns into a different state showing a slight redshift of the absorption. This state is the activated state that transmits the allosteric signal for the biological responses.

The tyrosin (Tyr) and glutamine (Gln), which form a hydrogen bond network with the chromophore, are highly conserved and essential for the photoactivation. The recent studies have revealed that the photoactivation is achieved by the Gln flip, i.e. hydrogen bond switch, presumably via the electron transfer between the Tyr and FAD. This scheme has raised the question about how Gln flips after absorbing blue light. In this study, we take up a BLUF protein PapB from the purple bacterium *Rhodopseudomonas palustris*. Femtosecond stimulated Raman spectroscopy (FSRS) is used to examine the excited-state structural change of the chromophore, which is expected to reflect the FAD-protein hydrogen bond dynamics in the course of the photactivation process.

Figure 1 shows the FSRS spectra in the high frequency region (900-1750 cm^{-1}) after the photoexcitation at 450 nm ($S_1 \leftarrow S_0$ transition). The S_1-state vibrations are resonantly enhanced by the Raman pump at 800 nm. The observed resonance Raman bands decay without showing any frequency shift or relative intensity change during the excited-state lifetime (~60 ps). This indicates the negligible structural change of the excited-state chromophore in the protein cavity.

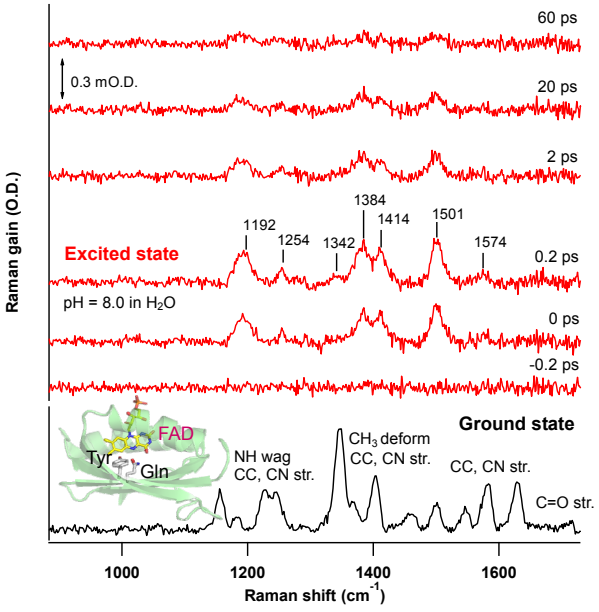

Figure 1: FSRS spectra of PapB excited/ground states

In the presentation, we will also present the low frequency dynamics of the chromophore. The excited-state structural dynamics in the active site of PapB is discussed.

Two-dimensional heterodyne-detected vibrational sum frequency generation spectroscopy of water at a charged interface with excess salt

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Dynamics of the interfacial water associated with salts at a charged interface has been studied by a newly developed Two-Dimensional Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy (2D HD-VSFG) technique [1,2]. It was found that the vibrational dynamics of the interfacial water becomes substantially slow in the presence of excess salt.

Figure 1(a) shows the 2D HD-VSFG spectra of OH stretching of water at a positively charged CTAB interface with 0.5 M NaCl at 0 fs delay time, and figure 1(b) shows the vertically sliced spectrum of 2D HD-VSFG, which represents the $\Delta \mathrm{Im}\chi^{(2)}$ (change in second order nonlinear susceptibility) spectra of different pump frequencies. These data clearly show that with addition of NaCl, OH stretching of water shows a narrow bleach feature above 3450 cm^{-1} excitation but a broad bleach feature appears below that excitation. The narrow bleach feature above 3450 cm^{-1} pump can be assigned to the water molecule hydrating an anion in which one of the OH is hydrogen bonded directly to Cl^- (O-H…Cl^-). The broad bleach feature below 3450 cm^{-1} is ascribable to water molecules forming O-H…O hydrogen bonding with each other. Spectral diffusion of water associated with salt takes ~400 fs whereas it takes only 100fs without salt. This clearly demonstrates that the vibrational dynamics of the interfacial water becomes substantially slower in the presence of excess salt.

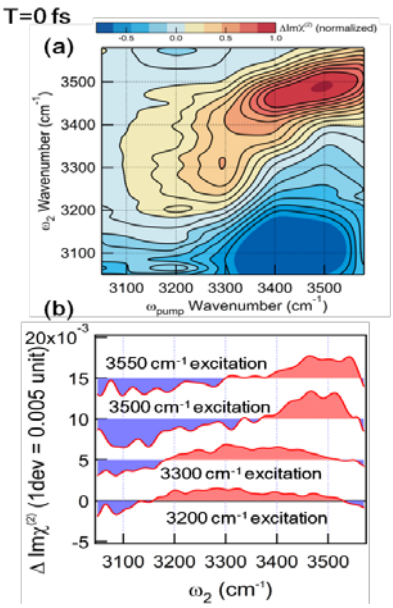

Figure 1. (a) 2D HD-VSFG spectrum of water at the charged interface with 0.5 M NaCl for 0 fs delay time. **(b)** $\Delta \mathrm{Im}\chi^{(2)}$ spectrum for different pump frequencies obtained by vertical slicing of the 2D HD-VSFG shown above.

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Fullerene Excitons Reveal Morphology of Polymer:Fullerene Blends

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Morphology of the bulk heterojunction – that is, the nanoscale texture of polymer and fullerene constituencies – is one of the keys for optimizing efficiency of plastic solar cells [1]. Morphology is a challenging property not only to control but even to characterize as this generally requires chemical selectivity combined with 10-nm spatial resolution.

Here we show how to get hold on sample morphology in an all-optical way, making use of *fullerene excitons* [2]. Our approach is based on the fact that soluble fullerene derivative [70]PCBM, currently used in overwhelming majority of novel organic photovoltaic blends, exhibits a substantial visible light absorption. First, a pump pulse selectively creates an exciton in the [70]PCBM domain which after diffusion to the interface dissociates into a hole in polymer and electron in the fullerene (Fig.1a). The hole modifies the vibronic structure of the polymer leading to the so-called polaron absorption which is probed by a delayed IR pulse. From the delay of the IR response and efficiency of exciton-hole formation (Fig.1b), a characteristic size of the [70]PCBM domains can be retrieved (Fig.1c). In this way, valuable information on morphology can be obtained "on-the-fly" in working photovoltaic devices.

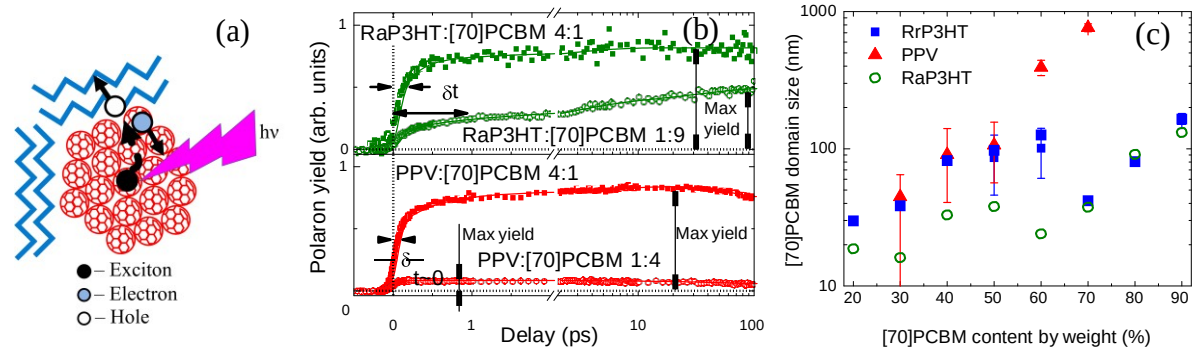

Fig.1. (a) Schematics of the proposed approach; (b) exciton dissociation dynamics; (c) [70]PCBM domain size dependence in various blends. In (c), closed and open symbols represent the measured (by AFM/TEM) and retrieved values, respectively. RrP3HT and RaP3HT stand for region-regular and region-random P3HT. Note substantial differences of the domain size in blends with different polymers.

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Three dimensional infrared spectroscopy of ice Ih

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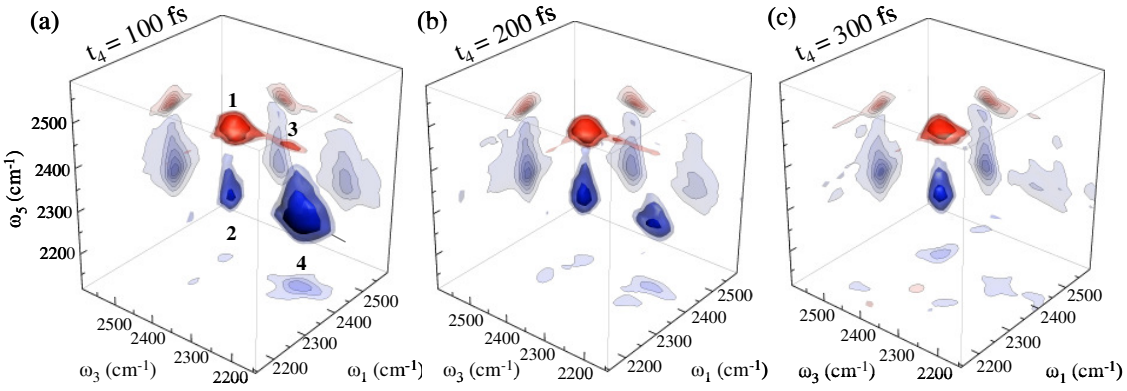
Energy transfer in ice Ih is investigated experimentally using three-dimensional infrared (3D-IR) spectroscopy [1]. The OD stretch mode of isotope diluted ice Ih (5% HOD in H_2O) is used to deposit energy by successive femtosecond pulse excitations in the mid-IR.

The 3D-IR response reveals four distinct peaks, which results from the change of population on the v = 0, 1 and 2 vibrational states. The lineshape distortion, previously observed with 2D-IR spectroscopy, relates to contributions from the low frequency intermolecular modes [2] and appears significantly enhanced as one climbs higher up the vibrational ladder. Additionally, the signal from the population decay of v = 2 state decays much more rapidly (<100fs) than the corresponding response from v = 1.

Quantum dynamic simulations reproduce qualitatively the lineshape features observed in the experiment, as well as the dynamical evolution of the vibrational states. The origin of the rapid decay of the v = 2 state is traced to nonadiabatic effects between vibrational states, leading to very efficient and ultrafast energy transfer, as well as to partial hydrogen bond dissociation [3].



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[3] F. Perakis, J. Borek, P. Hamm, manuscript in preparation

Parallel Relaxation Pathways of Malachite Green Revealed by Ultrafast Pump-Dump-Probe Spectroscopy

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Malachite green (MG) is one of triphenylmethane dyes that are well-known to undergo ultrafast relaxation upon photoexcitation. So far, it has been argued that the relaxation dynamics can be described by a sequential model in which the excited-state molecule relaxes to the ground state through an intermediate state (S_x) [1, 2]. However, there still remain a lot of disputes about the S_x state such as its assignment and how it is generated. To clarify the relaxation pathway, we studied the ultrafast relaxation dynamics of MG using pump-dump-probe spectroscopy.

The blue curves in Figure 1 show transient absorption spectra of MG at 1 ps and 4 ps, representing the S_0 bleaching (the negative band) and the S_x absorption (the positive band). When we applied a 950-nm dump pulse at 0.6 ps after photoexcitation, the S_0 bleaching at Δt=1 ps is drastically decreased as shown by the red curve. It indicates that the S_1 population is effectively transferred back to the S_0 state by the dump pulse through the $S_1 \rightarrow S_0$ stimulated emission transition. Surprisingly, we found that the S_x absorption was not affected by the dump pulse as no spectral change was observed at Δt=4 ps. This observation apparently conflicts with the sequential relaxation scheme, because in that scheme the S_1 molecule is the precursor of the S_x state and hence the decrease in the S_1 population should lead to a decrease of the S_x population as well. To rationalize the experimental results, we propose a new relaxation scheme that involves parallel relaxation pathways. In the presentation, we discuss the relaxation pathways of this prototypical molecule further in detail based on the dump-wavelength dependence of the transient signals.

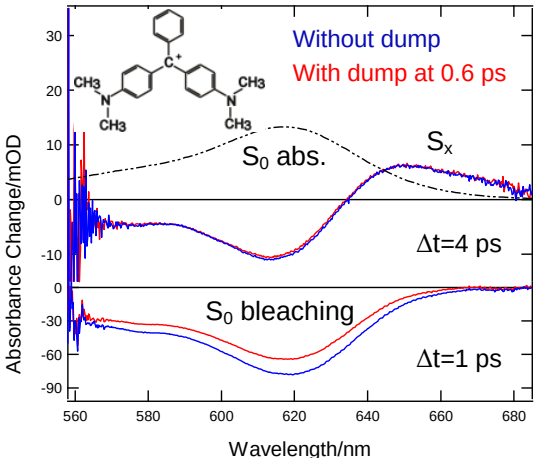

Fig. 1 Transient absorption spectra of malachite green at 1 ps (lower) and 4 ps (upper) measured with (red)/without (blue) the 950-nm dump pulse (pump-dump delay is 0.6 ps).

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PB8

In situ monitoring of a protein folding process on the artificial lipid bilayer by Surface Enhanced Infrared Absorption Spectroscopy

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Surface Enhance Infrared Absorption (SEIRAS) have unique properties that enhances signals at vicinity (in an order of several nm's) of a substrate metal. This property is useful to determine solely the surface chemical process distinguished from that occurred in bulk phase. Therefore when a biological sample of interest is confined to such surface, one can selectively monitor a chemical reaction of the target regardless of the complex ensemble biological process in the bulk phase. We present an application of SEIRAS to *in-situ* investigation for a folding process of membrane protein (bacteriorhodopsin) during cell free expression on the nano-disc artificial lipid bilayer.

Figure 1 A presents a scheme of the experiment with SEIRAS set-up. Single reflection attenuated total reflection (ATR) configuration with gold thin film at reflective surface allows free exchange of the test samples in the bulk phase during measurement of the IR spectra. Surface of SEIRA active gold thin film is modified by an artificial lipid bilayer framed by an amphiphilic scaffold protein (nanodisc). The nanodisc is bound through recombinant affinity tags at the scaffold protein with surface modified Ni-NTA self-assembled monolayer. Mixture of all components for the cell-free expression of bacteriorhodopsin (*bR*) except translational factor (DNA plasmid) are incubated in the bulk phase at the beginning of the measurement. As the translational factor is added to the mixture, protein synthesis and the folding start to process (Figure 1 B). This process had been monitored by SEIRAS in time resolved manner (Figure 1 C). From these spectra we had succeed to monitor individual reaction step of the translation of *bR* into the surface confined lipid bilayer.

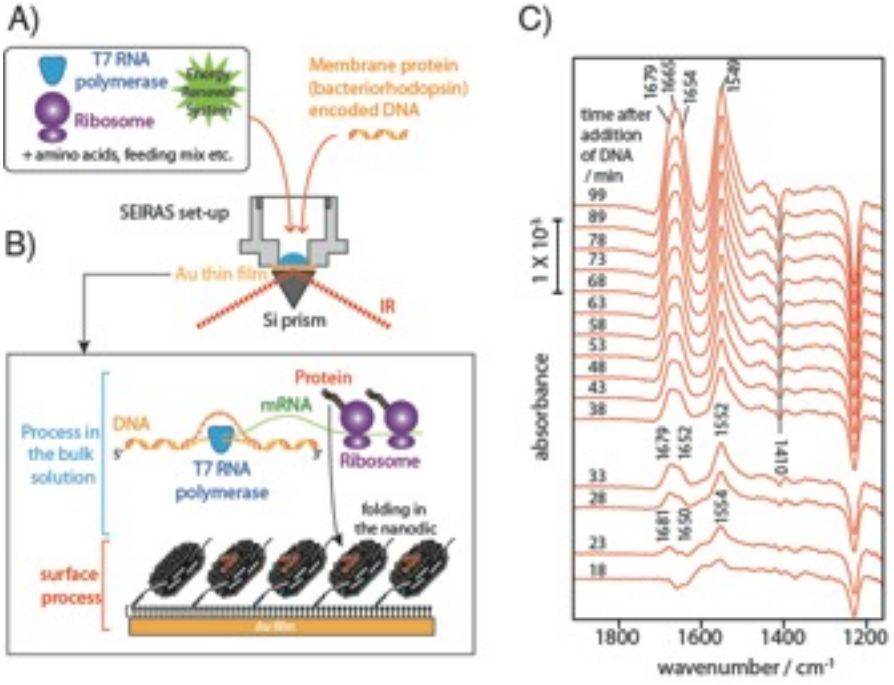

Figure 1 A) A scheme of the experiment and SEIRAS optical setup; B) In vitro translational process on the gold surface; C) SEIRA spectra observed during the folding of *bR* into the surface tethered nanodisc monolayer.

Chemical exchange between phenol and phenol-benzene complex observed by 3D IR spectroscopy

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We present a 3D IR experiment [1] on the dynamics of exchange between free phenol and a phenol/benzene complex at thermal equilibrium [2]. 3D IR is an extension of 2D IR into a third frequency dimension – it is a technique that allows correlating infrared spectra during two population times, t_2 and t_4, enabling to measure the three point frequency-frequency correlation function. Various combinations of the two population times are measured in order to investigate whether the process is Markovian, or if some residual memory persists at a picosecond timescale. Hence, for the system of study, we are interested in whether the three point frequency-frequency correlation function, dependent on both t_2 and t_4, reduces to a two point correlation function, dependent on the sum of $t_2 + t_4$ only.

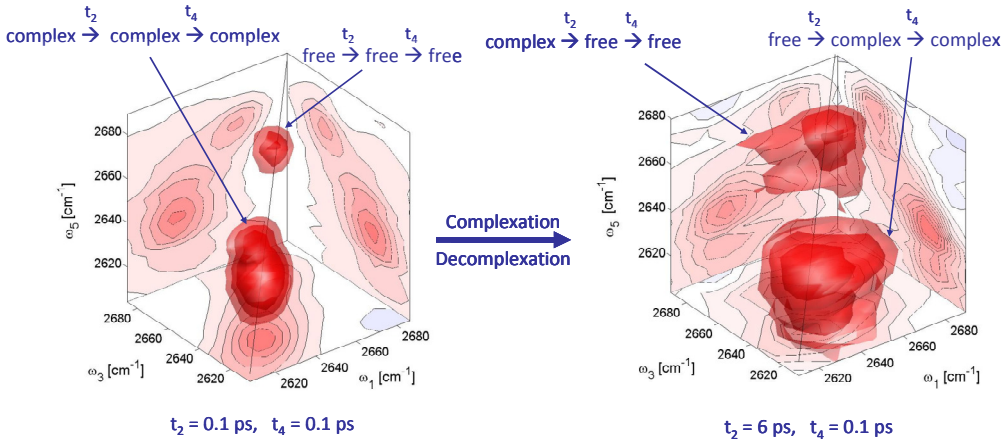

Fig. 1 Example 3D IR spectra of phenol in benzene/CCl_4 mixed solvent (3:40:100 molar ratios). At short population times only two diagonal peaks corresponding to the free phenol and phenol/benzene complex are present. At longer population time t_2, cross-peaks appear, indicating complexation of the free phenol and decomplexation of the phenol/benzene complex during t_2. Cross-peaks were also observed with varying t_4 or t_2 and t_4 simultaneously.

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Ligand Binding Studied by 2D IR Spectroscopy Using the Azidohomoalanine Label

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Binding of a peptide ligand (RAGEF2) to an allosteric protein (PDZ2) is studied using 2D IR spectroscopy and the unnatural amino acid Azidohomoalanine (Aha) [1]. Aha is an interesting label in IR spectroscopy, because the central frequency is in a non congested part of the spectrum (~2100 cm^{-1}) and shifts depending on its local environment [2]. Aha can be incorporated in peptides and protein using chemical synthesis or biochemical methods.

Depending on the position of the mutation 2D IR spectra of bound and unbound peptide, where a single amino acid has been mutated to Aha, differ in central frequencies and line shapes. Time resolved measurements of one mutant (Val(-3)Aha) reveal that the spectral diffusion has a fast (~3 ps) and a static component when the peptide is bound to the protein, whereas the static component is missing when it is unbound.

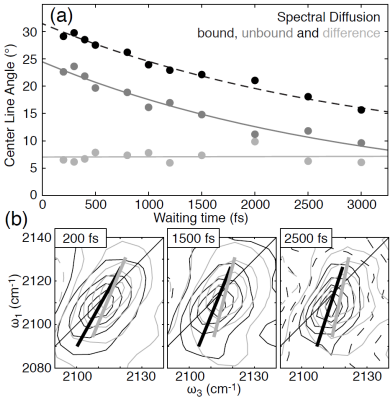

Fig. 1 Val(-3)Aha bound (black) and unbound (grey) to Protein.

This observation can be explained with the X-ray crystal structure of the unlabeled peptide where the mutated amino acid is in contact with the protein and not fully solvent exposed. Thus, we demonstrated that Aha can be used as a label in 2D IR to obtain site-specific information of the binding of peptides and proteins.

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Quantum decoherence in vibrational nonadiabatic transitions of water studied by quantum-classical molecular dynamics simulations

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Non-adiabatic vibration transitions are ubiquitous in condensed phase systems and essential, *e.g.* in vibrational energy transfer. Computational studies of these phenomena usually employ a mixed quantum-classical scheme in which one part of the system is treated quantum mechanically while the rest is described as a classical bath. A resulting key limitation lies in the neglect of the bath wave function. In particular, the loss of phase coherence within the quantum system due to interactions with the bath is not properly described. This can be corrected by an explicit consideration of quantum decoherence, involving the calculation of the diverging paths followed by the classical bath interacting with different quantum states. For electronic non-adiabatic transitions, the proper inclusion of decoherence was shown to yield significant differences in the energy transfer rate constants[1].

Here we focus on vibrational decoherence. Following the approach pioneered for electronic transitions[1], decoherence is determined from Fermi's golden rule using mixed quantum-classical simulations and the frozen Gaussian approximation for the bath wave function. We apply this method to vibrational decoherence in liquid water, where it has been suggested that vibrational energy transfer changes from a coherent regime to an incoherent one with increasing temperature[2]. We determine the vibrational decoherence time for the OH stretch of HOD in D_2O and study its impact on the calculated infrared spectrum.

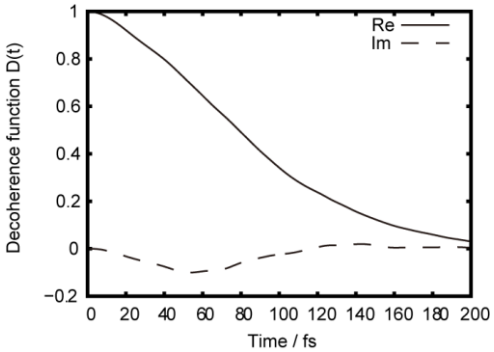

Fig. 1 Decoherence function for the OH stretch of HOD :D_2O.

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Two-Dimensional Raman-THz Spectroscopy of Water

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Water is a complex liquid, with the dynamics of the hydrogen-bond network lying at the bottom of its peculiarities. The associated low-frequency spectrum of water consists of broad bands at ~600 cm^{-1} (hindered rotations), ~200 cm^{-1} (hydrogen bond stretching) and at ~50 cm^{-1} (hydrogen bond bending). However, the broadening mechanism of these bands and the couplings between them are not yet understood. To resolve the lineshape functions of these modes, a 2D spectrum directly in this frequency range is needed. Here, we demonstrate a hybrid 2D-Raman-THz spectroscopy that circumvents experimental problems of 2D-Raman and 2D-THz spectroscopy. This experiment paves the way towards investigating the lineshape functions and couplings concerning low-frequency intermolecular degrees of freedom of water.

The experimental water 2D-Raman-THz time-domain response (Fig. 1) shows interesting features beyond the instrument response function and its convolution with the simulated response function [1]. The signal is dependent on the relative polarizations between the Raman and THz pulses, as indicated by the simulations [1]. The intensity dependence measurements (Fig. 1b, inset) show that the signal is linear with respect to the Raman pulse energies, indicating that the signal is due to a Raman process. The absence of solvated electrons was further verified using 800-800 nm transient absorption spectroscopy.

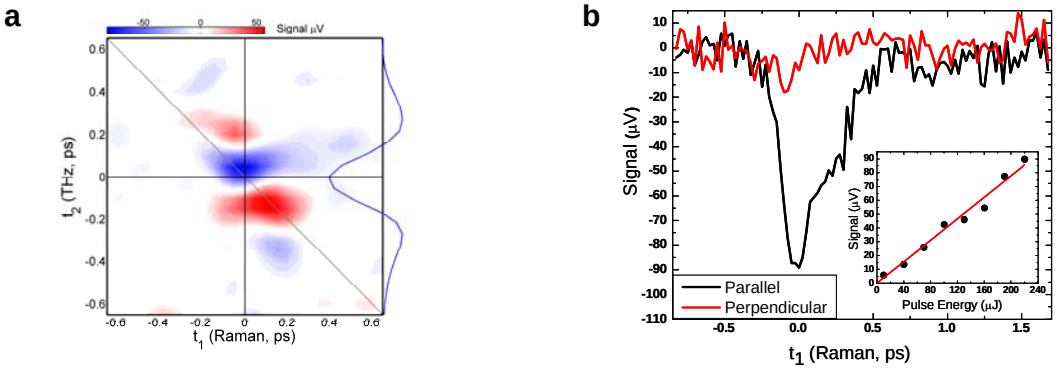

Fig. 1. 2D-Raman-THz signal of water (a). A 1D scan along the Raman pump delay (t_1) with parallel and perpendicular Raman and THz field polarizations (b). Intensity dependence of the peak of the signal (b, inset).

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Ultrafast dynamics of excited state DNA probed by femtosecond stimulated Raman spectroscopy

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The ultrafast dynamics of excited state DNA following UV excitation was observed by femtosecond stimulated Raman spectroscopy (FSRS). FSRS has been a greatly promising technique to probe such ultrafast event with high spectral resolution. Here, we made efforts to observe transient stimulated Raman signals from photoexcited DNA monomers with femtosecond time resolution. Multiple Raman pump pulses covering from UV to visible energy regions were generated by utilizing high pressure hydrogen gas Raman shifter with a 400 nm picosecond pulse. Taking advantage of resonance enhancement of Raman signals, UV Raman pumps at 300 and 343 nm are able to probe the vibration cooling process of the hot ground state while visible Raman pumps at 480 and 600 nm can potentially probe vibrational dynamics from excited state DNA.

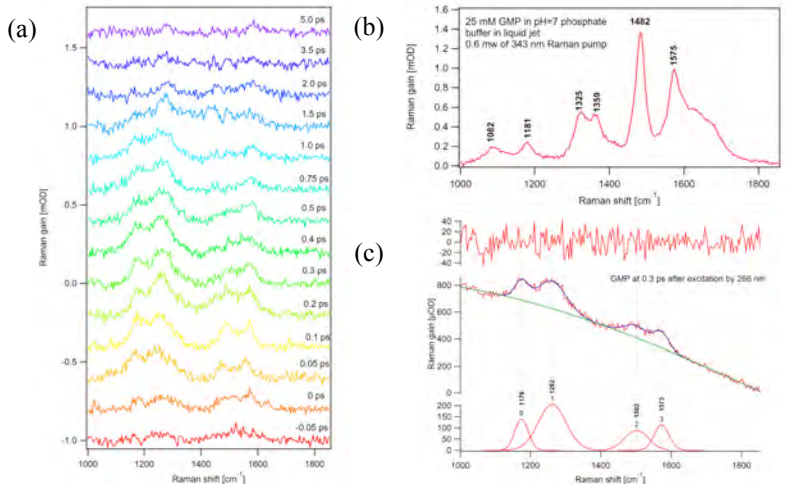

Figure 1. (a) Time-resolved FSRS spectra of transient state GMP upon excitation at 266 nm pulse. (b) Ground state FSRS spectrum of GMP. (c) Transient FSRS spectrum of GMP at 0.3 ps after the excitation, fitted by Gaussian and polynomial lineshapes.

As shown in Figure 1, Time-resolved FSRS spectra of guanosine 5'-monophosphate (GMP) in aqueous buffer solution were collected using 343 nm Raman pump for comparison with 2'-deoxyguanosine 5'-monophosphate (dGMP). The observed Raman signals were attributed to be mostly from hot ground state because of their consistent red-shifting from ground state vibration modes. However, a signal at 1500 cm^{-1} is considered to be from excited state due to its faster dynamics than the hot vibrational signals. Current experiments are incorporating a 600-nm Raman pump in order to resonantly enhance the Raman signal of the $\pi\pi^*$ excited state via its visible transient absorption band.

Excited state dynamics for thymine by using sub-10 femtosecond deep ultraviolet pump and probe pulses

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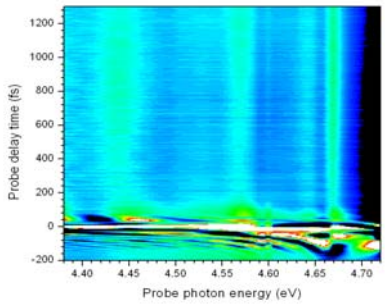

Fig.1 Two dimensional absorption difference.

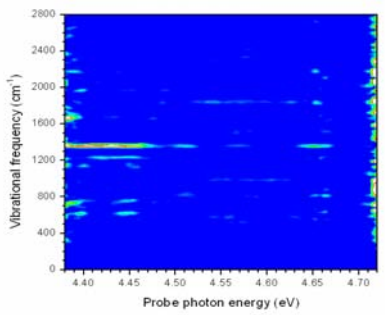

Fig.2 Two dimensional of FFT power spectrum.

A deep ultraviolet (DUV) laser system was demonstrated by using four-wave mixing technique in argon gas filled hollow fibers[1, 2]. An ultrafast few cycle DUV pulse was achieved with pulse width of 9.8 fs and output power over 250 nJ. And the spectrum range covered from 260 nm to 285 nm. By using this DUV pulse laser system; real time vibrational spectrum for Thymine was observed by pump probe experiment (Fig.1). The sample was dissolved in distilled water with the concentration at 5.3×10^{-3} mol/L.A circulation cell with 0.3 mm thick CaF_2 window was used. , to avoid the photo damage, the optical path was set as shortest as 0.18 mm to avoid dispersion for DUV pulse in samples. For the result, four most intense vibrational modes with frequencies at 626, 772, 1244, 1366 cm^{-1} was observed in the calculeted FFT spectrum (Fig.2). Corresponding to ring defromation, C=O bending, ring streching, C-CH_3 streching, respectively[2, 3]. And their vibrational dephasing time were also calculated to be 272, 277, 296, 305 fs, respectively.

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Picosecond protein response to the chromophore isomerization in microbial rhodopsins

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Microbial rhodopsins are typical photoreactive proteins. A retinal chromophore is covalently bound to the lysine residue *via* a protonated Schiff base linkage. Photoisomerization of retinal induces sequential changes in protein structure, thereby facilitating their functions. We carried out picosecond time-resolved ultraviolet resonance Raman (UVRR) measurements on protein dynamics of ion-pump rhodopsins (bacteriorhodopsin and halorhodopsin) and photosensors (sensory rhodopsin I, sensory rhodopsin II, and *Anabaena* sensory rhodopsin) to clarify how fast protein moiety responds to the chromophore isomerization.

Time-resolved UVRR spectroscopy helps determine the structural dynamics at specific sites by selectively enhancing vibrational bands of aromatic amino acid side chains. For all microbial rhodopsins described above, we observed spectral changes of tryptophan bands in the picosecond region, in which the photoisomerized ground-state intermediate, named as K, is formed [1-3]. The band intensity bleached in response to retinal isomerization. It recovered with a time constant of a few tens of picoseconds. This spectral change can be attributed to structural rearrangements of protein moiety around retinal chromophore. In the vicinity of retinal, three tryptophan residues are conserved for most of microbial rhodopsins. Our systematic studies on microbial rhodopsins elucidated that the rates of the protein response to the chromophore in the picosecond temporal region were very similar among the all proteins.

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Chromophore structures of photocycle intermediates in *Gloeobacter* rhodopsin: a resonance Raman study

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Gloeobacter rhodopsin (GR) is one of the microbial rhodopsins which functions as an outward light-driven proton pump. GR has a retinal chromophore surrounded by seven transmembrane helices. The retinal is bound to Lys257 residue via protonated Schiff base. When GR absorbs light, the retinal isomerizes from all-trans form to 13-cis form. After the isomerization, GR exhibits a photocycle reaction through several photointermediates, which are K, L, M, N, and O intermediates (Fig. 1A). In order to understand proton pump mechanism, it is important to reveal chromophore structures of the intermediates. In this work, we investigated chromophore structures of the unphotolyzed state and L and M intermediates of GR with time-resolved resonance Raman spectroscopy.

We observed C-C stretching, C=C stretching, and C=N stretching bands in the 1160-1230, 1530-1620, 1640-1660 cm^{-1} regions, respectively (Fig. 1B). These spectra were compared to those bacteriorhodopsin (BR), which is the most studied proton pump protein. We found that GR showed similar spectra as BR for the unphotolyzed state and the intermediates. This suggests that chromophore configurations of these states for GR resembled the counterparts of BR. In the unphotolyzed state and L intermediate of GR, C=N stretching and N-H bending vibrations downshifted upon deuteration, indicating that the chromophores of the unphotolyzed state and L intermediate of GR were protonated.

In the spectra of M intermediate, we found differences between spectra of GR and BR. These suggested the difference of retinal conformation between the two proteins and coexistence of another intermediate which has protonated Schiff base in GR.

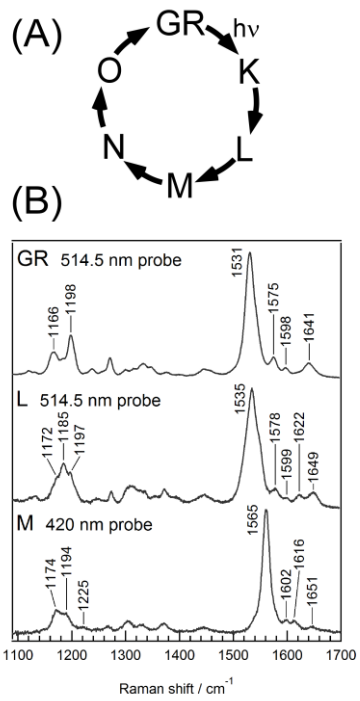

Fig. 1 Photocycle (A) and resonance Raman spectra (B) of GR

Ultrafast structural dynamics of membrane-bound water molecules revealed by two-dimensional surface-specific vibrational spectroscopy

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Lipid bilayer membranes constitute the external boundaries of cells and organelles and are composed primarily of amphiphilic lipid molecules that spontaneously form bilayers. The overall function of membranes relies on a subtle interplay between proteins, lipids and interfacial water. We investigate how the interaction between the lipids and water affects the structural dynamics of the water molecules. To this purpose, we study water in contact with a model lipid membrane (1,2-dipalmitoyl-3-trimethylammonium- propane (DPTAP)) using surface two-dimensional sum frequency generation (2D-SFG) spectroscopy with femtosecond time resolution. By full spectral modeling including spectral diffusion and the frequency dependence of the vibrational lifetime, we determine the frequency-frequency correlation function of the water O-D vibrations. We observe that lipid-bound water displays a remarkably fast decay of the frequency-frequency correlation function, showing a time constant of ~300 fs timescale (Fig. 1). The same decay time constant is observed for isotopically diluted (H-D exchanged) water near DPTAP. This latter result shows that the frequency fluctuations are not the result of Förster energy transfer between the water molecules, as previously observed at the water-air interface [1], but rather results predominantly from ultrafast fluctuations in the local environment of the membrane-bound water molecules.

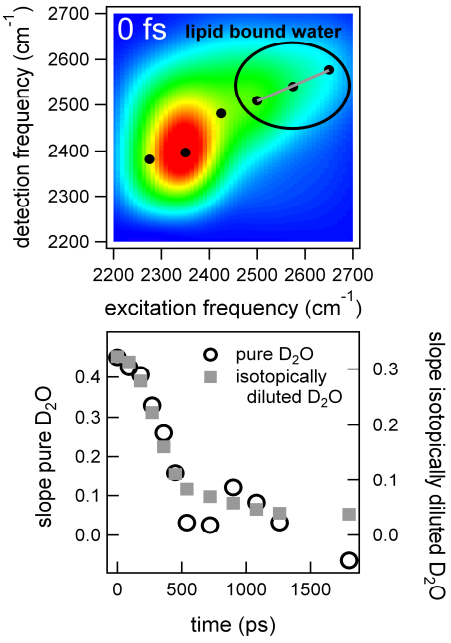

Fig. 1 top: 2D-SFG spectrum of D_2O at a DPTAP membrane; bottom: slope of the 2D spectrum as a function of delay time for D_2O and a mixture of D_2O and H_2O (1:2).

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Vibrational-Excitation Induced Proton Transfer in Nafion Nano-Channels

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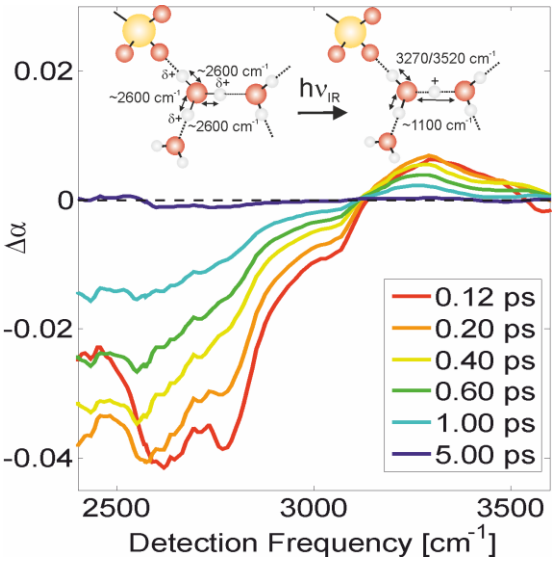
We study the properties of water molecules and protons in hydrated nafion nanochannels using polarization-resolved femtosecond vibrational spectroscopy. Nafion is a sulfonated tetrafluoroethelyne (Teflon)-based fluoropolymer and forms the most widely used proton exchange membrane (PEM) in hydrogen fuel cells. Excitation at frequencies between 2600 and 2900 cm^{-1} leads to a broad bleaching signal that corresponds to the excitation of one of the O-H stretch vibrations of an Eigen proton hydration structure (see figure). This structure consists of a central H_3O^+ ion, hydrogen bonded to water molecules and/or sulfonate groups of the nafion. The excitation also leads to a delayed rise of two induced absorption peaks at 3270 and 3530 cm^{-1}, corresponding to the O-H stretch vibrations of an $H_5O_2^+$ Zundel hydration structure [1]. The time dependence and anisotropies of the bands show that the excited ν=1 state of the proton vibration of the Eigen H_3O^+ ion evolves to the lower-energy ν=1 state of a symmetric O···H···O Zundel vibration, with a time constant of 170±20 fs. Simultaneously, the other O-H stretch vibrations of the H_3O^+ ion are turned into higher-frequency O-H stretch vibration of a water molecule flanking the Zundel proton. To our knowledge, this IR-induced proton transfer is the first observation of a chemical reaction in the condensed phase following single-quantum vibrational excitation. The reaction closely follows the adiabatic proton transfer mechanism as proposed by Hynes et al. [2]. The reaction can occur in Nafion membranes thanks to the strong coupling between the high-frequency proton vibration and the hydration structure, and the relatively long lifetime of the proton vibration in Nafion nanochannels (T_1=350 fs), compared to bulk liquid water (T_1=110 fs).



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Towards unraveling the mechanism of an anti-tuberculosis drug target

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Isoniazid (INH, C_5H_4N-CO-NH-NH_2) has been the therapeutic of choice for the treatment of *Mycobacterium tuberculosis* (Mtb) for over 60 years. However, despite widespread use, very little is documented about its mode of action. The recent emergence of INH-resistant mutations of Mtb has prompted great interest in unraveling the mechanism behind this enhanced resistance. INH is known [1] to inhibit InhA; an NAD(H)-dependent enzyme in Mtb which is required for the biosynthesis of mycolic acids, the long chain fatty acid components that form an essential component of the Mtb cell wall. The inhibition of InhA requires the activation of the pro-drug form of INH via biochemical oxidation which covalently binds to NAD(H). Here, we employ pulsed Fourier Transform 2D-IR (Fig. 1) and IR pump-probe methods to investigate the vibrational dynamics and spectroscopy of the precursors of the InhA inhibition: NAD(H), INH, InhA and the INH-NAD(H) adduct. These results provide new insights into the structure and solvation dynamics of these biologically relevant molecules.

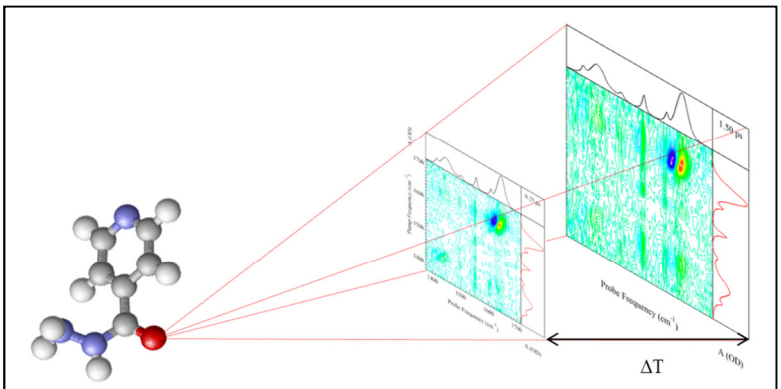

Fig. 1: 2D-IR spectra of pro-drug INH at 0.25 and 1.5 ps.

Reference:

[1] D. A. Rozwarski, G. A. Grant, D. H. R. Barton, W. R. Jacobs Jr and J. C. Sacchettini, Science **279** (1998) 98.

Theoretical study on frequency fluctuation and energy relaxation of HOH bend in liquid water

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Water is one of the most common liquids on the earth. It shows, however, a lot of anomalous thermodynamic properties. All of the anomalous properties arise from strong hydrogen bonds (HBs). To examine the HB properties, the detailed dynamics, i.e. the frequency fluctuation and energy relaxation, of the OH stretch have been investigated by using the nonlinear spectroscopy techniques and theoretical calculations. In contrast, the frequency fluctuation and energy relaxation of the HOH bend have not been well examined, thus, the HOH bend is less understood than the OH stretch. We investigate the dynamics of the HOH bend in liquid water by using molecular dynamics (MD) simulations with *ab initio*-based water model potential, TTM3-F. The theoretical calculation of the two dimensional IR spectra shows ultrafast spectral diffusion of the HOH bend with the time constant of 100 fs. We find that the ultrafast frequency fluctuation of the HOH bend is due to the strong coupling between the HOH bend and the OH stretch as well as the intermolecular HB bend. We also study the intramolecular and intermolecular energy relaxation process in liquid water with non-equilibrium MD simulations. The calculated relaxation times from the OH stretch to the HOH bend and that from the HOH bend to intermolecular motions are 300 and 200 fs, respectively, which are in good agreement with the experimental results. The detailed mechanism will be discussed in the presentation.

PB21

Thermochemical solar energy capture via photoisomerization of dimetallic fulvalene complexes

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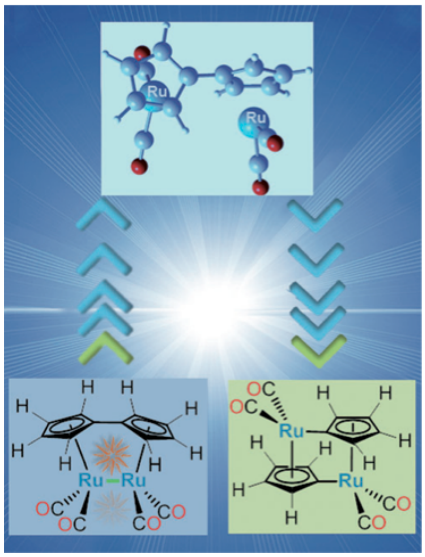
Amid the ongoing efforts to develop methods for the capture and storage of solar energy, thermochemical batteries capable of harnessing energy in the form of reversible chemical reactions are receiving significant attention. In this spirit, we are using time-resolved infrared spectroscopy (TRIR) as part of our ongoing investigation into the use of photochromic dimetallic fulvalene complexes as potential targets for solar energy storage complexes. Light from the solar spectrum can readily induce photoisomerization, storing as much as ca. 20 kcal/mol of energy, which can also be rapidly released with the use of an appropriate catalyst. In a study combining TRIR and X-ray transient absorption spectroscopies and density functional theory calculations, we elucidated the role of a key triplet intermediate in the photoisomerization of ruthenium based complexes. Even more recently we have carried out an investigation into the photoisomerization of a most cost-viable iron analogue and discovered that the absence of this key triplet intermediate in the iron congener prevents photoisomerization in the species studied. Ongoing research is focused on investigating related complexes with the potential for solar energy storage, with a focus on developing cost-effective dimetallic fulvalene complexes.



PB22

Exciton Delocalization and Dynamics in Helical π-stacks of Self-assembled Perylene Bisimides

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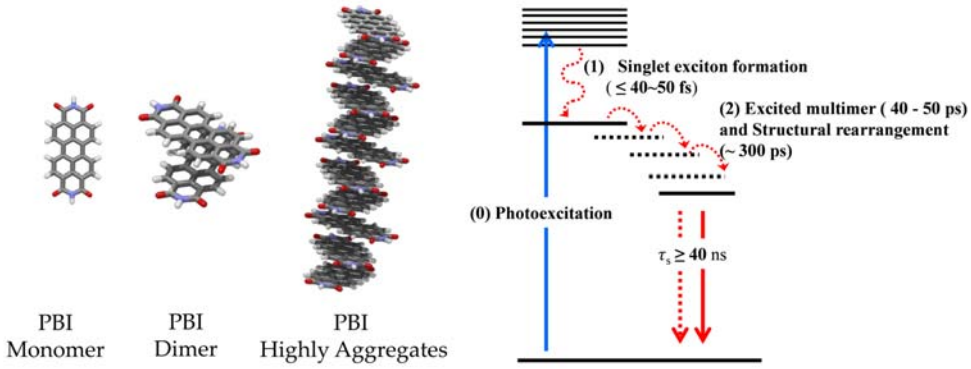
We have explored the exciton dynamics and excited-species formation processes in columnar helical aggregates of planar PBI dyes by various spectroscopic techniques such as time correlated single photon counting and femtosecond pump–probe measurements with anisotropy changes. The outcome of this study is that photogenerated excitons in helically stacked PBI dyes experience complicated relaxation processes that involve excited-state interactions such as exciton delocalization and excimer formation. The comparative study revealed that the excited-state interactions in the large-sized helically stacked aggregates extend beyond two PBI units, leading to a final excimer trap state within ~50 ps. Although in competition with this relaxation path into the excimeric trap state, exciton diffusion has been revealed by exciton–exciton annihilation processes, occurring at high excitation power. We can conclude that the exciton diffusion can reach a length of about 10 monomer units. This result shows that columnar PBI stacks might still be useful for optoelectronic applications if the relaxation process leading to excimer traps is prevented, e.g. by structural modifications of the molecules.



References:

[1] J. M. Lim, P. Kim, M. -C. Yoon, J. Sung, V. Dehm, Z. Chen, F. Würthner, D. Kim.,

Relationship Between Exciton Delocalization and Excited-State Conformational Dynamics in Linear and Cyclic π-Conjugated Oligothiophenes

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Understanding the complex nature of charge and energy transfer is an essential component in designing and optimizing the rich array of organic electronic devices. However, organic semiconductors fundamentally differ from their inorganic counterparts by having a significantly stronger electron-phonon coupling. In this regard, we have investigated the influence of nuclear geometric relaxation on the extent of the excited-state electronic delocalization in π-conjugated linear and cyclic oligothiophenes using methods of femtosecond time-resolved fluorescence upconversion [1].

Anisotropy measurements show that light absorption generates an excited state is initially strongly delocalized along the oligothiophene but contracts rapidly following vibrational relaxation of the nuclei along C-C stretch coordinates on the subpicosecond time scales. We also demonstrate that interporphyrin torsional relaxation leads to a subsequent increase in the excited-state electronic delocalization on a relatively longer time scale (~30ps). These results therefore indicate that, following excitation, the initially highly delocalized excited-state first contracts and then expand again along the conjugated backbone in accordance with the time periods for the vibrational modes coupled to the electronic transition.

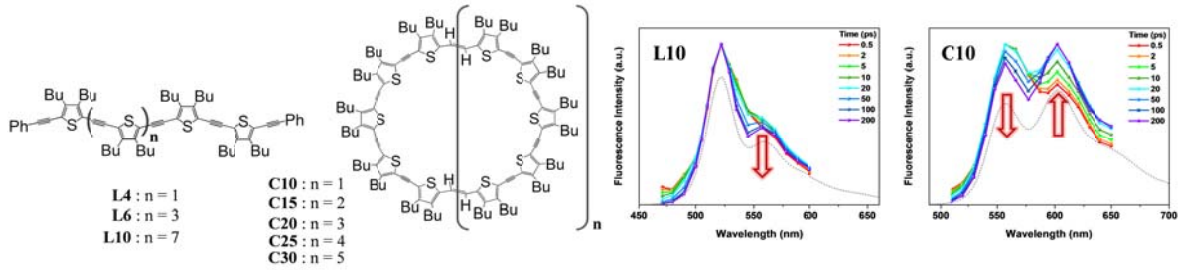

Fig. 1 Molecular structures of linear and cyclic oligothiophenes (left) and time-resolved fluorescence spectra of **L10** and **C10**, respectively (right).

Reference:

[1] M. Iyoda, J. Yamakawa, and M. Jalilur Rahman, *Angew. Chem. Int. Ed.* **50** (2011) 10522.

PB24

Vibrational Relaxation in RNA Nucleotides following Electronic Excitation

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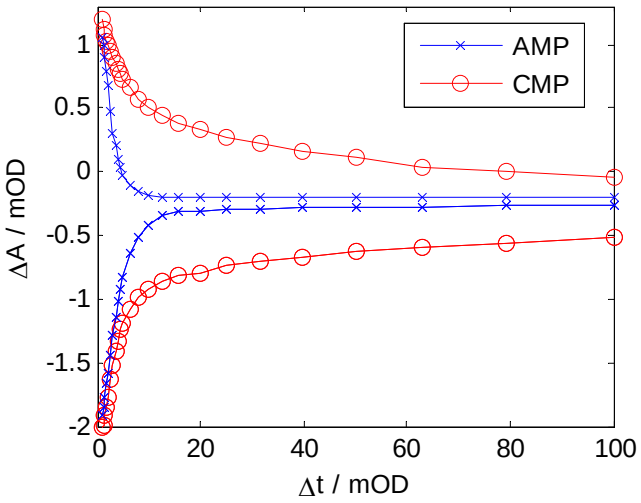
The resistance of DNA to photo induced mutation is critical to understanding the early evolution of life. We use the RNA mononucleotides adenosine 5'-monophosphate, (AMP), and cytidine 5'-monophosphate, (CMP), in aqueous solution as model systems, measuring the vibrational response to UV excitation.

When irradiated with 266 nm photons, the strong π→π* transition in AMP and CMP is excited. The ππ* excited states exist for less than 1 ps[1]. In AMP, internal conversion *via* conical intersection (CI) to the electronic ground state occurs in 260 fs, converting the electronic excitation energy to vibrational energy. The vibrational energy is dissipated to the surrounding water molecules in 3.8 ps. In contrast, for CMP, the deactivation of the ππ* state goes through an electronic state of nπ* character[2]. We observe a transient signal with a lifetime of 33 ps, and assign it to absorption by this nπ* state[3]. The relatively long lifetime suggests that the CI between the nπ* state and the ground state is not as easily accessible as the CI between the ππ* state and ground state in AMP.



Inside a living cell, DNA is not in a strict aqueous environment. The double helix structure has every DNA base surrounded by other DNA bases. To examine more closely the vibrational dynamics in such a non-aqueous environment, we plan to perform an experiment with DNA in an organic solvent.

References:

[1] J. Pecourt, J. Peon, and B. Kohler, J. Am. Chem. Soc. **122** (2000), 9348.
[2] P. M. Hare, C. E. Crespo-Hernández, and B. Kohler, PNAS, 104 (2007), 435.
[3] J. B. Nielsen, J. Thøgersen, S. K. Jensen, and S. R. Keiding, Chem. Phys. Lett., submitted.

Vibronic relaxation dynamics in multiphoton reactions of indocyanine green in ethanol

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Control of reaction by light is one of the central themes of chemistry. Cyanine dyes serve as model compounds and great effort has been dedicated to understanding reaction dynamics at S_1 state. Recently, we found that the reaction efficiency of the trans-to-cis photoisomerization of indocyanine green (ICG) in ethanol drastically increased by exciting ICG molecules by four-photon process of a femtosecond near infrared (NIR) pulse resonant to the $S_1 \leftarrow S_0$ transition [1]. In this paper, we describe the vibronic relaxation dynamics at intermediate states of the multiphoton process by ultrafast transient absorption measurements.

Figure 1 shows the NIR-UV two pulse correlation of transient absorption by ICG cis-isomers. In the figure, the result of the least square fit to a model function is also shown. The model function was a convolution between the time profiles of pump pulses and exponential decay functions corresponding to the relaxation at intermediate states. In both positive and negative decay regions, the traces were well reproduced by the combination of two decay components. The time constants of the decay components were 1.0 and 0.1 ps, respectively. The former time constant is consistent with the reported lifetime of S_n state reached by NIR two-photon process [1]. The amplitude of the fast decay component (0.1 ps) was almost proportional to the UV pump fluence. This result indicates that the fast decay component represents relaxation dynamics on S_n state, and the 0.1 ps time constant suggests that the fast decay represents the vibrational relaxation on S_n state. The relatively large amplitude of this fast decay component indicates the importance of vibrational excitation on S_n state for the multiphoton process. In the presentation, the vibrational relaxation dynamics at lower electronic excited states will be also described.

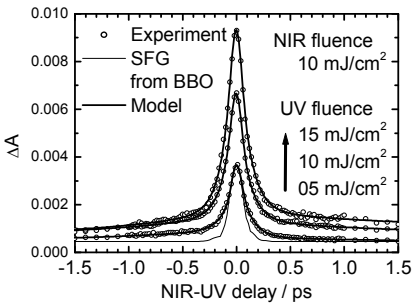

Fig. 1 Two-pulse correlation traces of absorbance change by ICG cis isomers.

References: [1] M. Fuyuki et al., Chem. Phys. Lett. **499** (2010) 121; Chem. Phys. Lett. **511** (2011) 121 45; J. Photochem. Photobiol. A. **252** (2013) 152.

The influence of hybrid orbital reconstruction on the mechanism of proton transfer in protonated benzene

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Proton transfer is one of the most fundamental processes in chemistry and biology. Proton transfer in fuel cells, hydrogen storage materials and biomolecules are typical examples. Recently, it has been pointed out that fast motion of hydrogen atoms is strongly coupled with slow motion of carbon atoms in organic molecules[1]. To clarify the effects of heavy atoms motion on the proton transfer dynamics, we chose proton transfer in protonated benzene (Fig. 1) as a model system and perform *ab initio* molecular dynamics simulations.

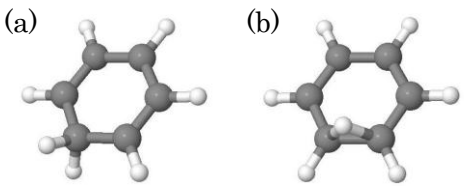

Fig. 1: Protonated benzene ($C_6H_7^+$)
(a) Stable state (b) Transition state

First, we examine the life time distribution which is the exsisting time of a transferring proton on one of carbon atoms in benzene ring, and it has been clearly shown that contribution of short-time trajectories is too large and non-statistical distribution appears. Detail analyses of trajectories suggest that proton is likely to stay between two carbon atoms. This is because there appears “dynamically stable state” which is caused by the strong coupling between fast proton motion and slow skeleton motion. The “dynamically stable state” is not a statistical minimum. The reconstruction of its hybrid orbital from sp^3 to sp^2 at a proton donner carbon slowly occurs and during this reconstruction, the “dynamically stable state” appears as the the limit of sudden approximation.

Because of the appearance of the “dynamically stable state”, the proton does not bind to any carbon atoms and moves back and forth around the middle point which is corresponding to the transition state. And then the ratio of short-time trajectories becomes higher in the life time distribution.

References:

[1] H. Ushiyama and K. Takatsuka, J. Chem. Phys., 115, 5903 (2001).

Water migration around peptide linkage in Acetanilide-(water) 1:1 cluster studied by time-resolved IR spectroscopy

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The interactions between molecule and solvent are manifold, e.g. dispersion forces, hydrophobic/hydrophilic interactions or hydrogen bonds can be mentioned. With regard to the importance in biological processes proteins are of great interest. The biological environment of proteins is strongly affected by water and the hydration has a strong effect on the structure (e.g. α-helix or β-sheet) and reactivity. One of the fundamental processes for growth and health of biological systems is the folding motion of proteins. This reconfiguration requires a rearrangement of the solvent molecules.

Acetanilide (AA) is one of the smallest aromatic molecules containing a peptide linkage and acts as a model substance for mass- and isomer selective investigation on a molecular level in the gas phase. In case of the water 1:1 cluster, a rearrangement of the solvent molecule induced by photoionization is observed.[1] In the S_0 state, the water molecule is either hydrogen-bonded to the CO or to the NH site of the peptide bond. In the cationic ground state (D_0) only the NH bound isomer is observed. By applying time resolved infrared (IR) spectroscopy, the migration dynamics was observed in real time and 5ps lifetime of the migration, role of intracluster vibrational redistribution (IVR) and existence of an intermediate have been revealed for the first time.[2]

The dependence of excess energy is an interesting point which should have a strong influence on the dynamics of the migration.

References:

[1] K. Sakota, S. Harada, Y. Shimazaki, H. Sekiya, *J. Phys. Chem. A* **2011**, *115*, 626.
[2] K. Tanabe, M. Schmies, A. Patzer, M. Schuetz, H. Sekiya, M. Sakai, O. Dopfer, M. Fujii, *Angew. Chem.-Int. Edit.* **2012**, *51*, 6604.

Dispersed three pulse vibrational photon echoes of N_2O in water and octanol: Model systems for phospholipids

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The ν_3 asymmetric stretch of N_2O is an excellent vibrational probe of solvent environments particularly for biological systems owing to its solubility in both hydrophobic and hydrophilic regions, large oscillator strength, vibrational frequency (2218 – 2230 cm^{-1}) and small, neutral hence minimally perturbing structure. In previous work rates of N_2O ν_3 vibrational energy relaxation were found to be a sensitive probe of the average structure of aqueous and non-aqueous regions of hydrated phospholipid bilayers [1]. Measurements in water and octanol N_2O solutions were crucial for developing an understanding of these rates in the hydrophobic and hydrophilic regions in these complex biological systems. The extension of ultrafast vibrational studies using this probe to the dephasing dynamics in these aqueous and non-aqueous environments is described here.

The transition frequency correlation function (FCF) of this "reporter" vibrational mode in H_2O and octanol have been determined by dispersed three pulse photon echo measurements. (See Fig. 1.) Dispersed measurements were required to eliminate background contributions and simplified the analysis. The FCF in H_2O only showed a 1.5 ps decay spectral diffusion component in addition to the rapid homogenous inertial contraibution. This fluctuation is identified with H-bond breaking time scale similarly found in azide echo studies. However, unlike the aqueous N_3^- results no long lived inhomogeneity is evident in the FCF. The corresponding FCF in octanol exhibits fluctuation components due to H-bonding of octanol clusters (3.3 ps) and the wagging motions of the hdrocarbon chains (35 ps).

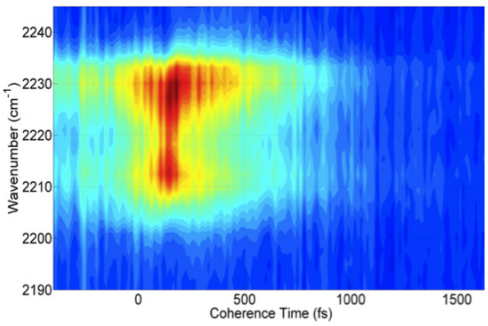

Fig. 1 Dispersed three pulse photon echo of the N_2O ν_3 mode in H_2O.

References:

[1] L. R. Chieffo, J. T. Shattuck, E. Pinnick, J. J. Amsden, M. K. Hong, F. Wang, S. Erramilli and L. D. Ziegler, J. Phys. Chem. B **112** (2008) 12776.

Molecular dynamics simulation for fast dielectric relaxation of hydrated ion

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Suzuki and co-worker observed dielectric spectra for aqueous solutions of alkali halide and of various proteins, such as actin filaments in the frequency range 0.2 - 26 GHz. The spectra involved a component higher than the peak related to the orientational relaxation of bulk water [1, 2]. The observation suggests that the dielectric relaxation of water in the hydration shell is faster than that of bulk water and named hyper-mobile water. On the other hand, it was difficult to show the fast relaxation by molecular dynamics simulations.

We derived a time-correlation $c_z^{[i]}(t)$ function for dielectric relaxation of water in the *i*-th hydration shell on the basis of linear response theory. We calculated dielectric relaxation of water around the ion using molecular dynamics simulations. Figure 1 shows that the dielectric relaxation $c_z^{[i]}(t)$ near the ion is faster than that of bulk, although the orientational relaxation $s_z^{[i]}(t)$ near the ion is slower. With the distance from the ion, the relaxation curves $c_z^{[i]}(t)$ and $s_z^{[i]}(t)$ get close to the bulk results. The ratio of the relaxation time between the fast component in the nearest hydration shell and that of bulk is about 60 - 80 %. This calculated ratio is consistent with that between the hyper-mobile water and bulk water in the experiments for alkali halide aqueous solutions [3].

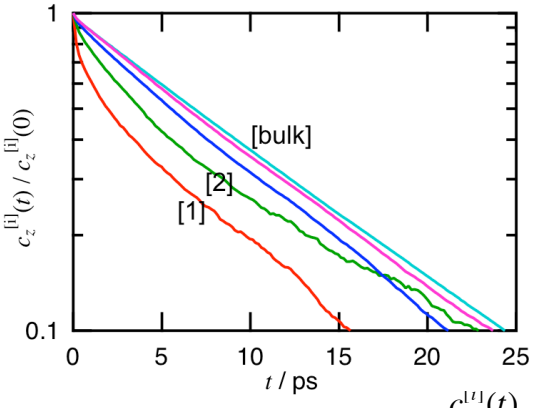

Fig. 1. Dielectric relaxation function $c_z^{[i]}(t)$ for the *i*-th hydration shell around ion.

References:

[1] S. Kabir, *et al.*, Biophsy. J. **85** (2003) 3154.
[2] T. Miyazaki, *et al.*, J. Phys. Chem. A **112** (2008) 10801.
[3] Y. Kubota, *et al.*, J. Chem. Phys. **137** (2012) 224502.

PB30

VIPER 2D-IR: chemical exchange beyond the vibrational lifetime and sub-ensemble selective photochemistry

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Femtosecond 2D-IR exchange spectroscopy (EXSY 2D-IR) allows to monitor the interconversion between molecular species in dynamic equilibrium [1]. To this end, one out of several coexisting species is vibrationally excited and the frequency change of the band induced by the interconversion is subsequently tracked. Observation of the exchange between species is therefore limited to the lifetime of the vibrational excitation, which usually is a few picoseconds. If the exchange is much slower, the evolution can thus not be tracked by EXSY.

Here we present a novel 2D-IR technique that overcomes this limitation by transferring the vibrational information to an electronic degree of freedom (Fig. 1, transition *A*): i.e. a UV/VIS pulse is chosen such that it is non-resonant for molecules in the vibrational ground state (arrow *C*) but becomes resonant for vibrationally excited molecules (VIbrationally-Promoted Electronic Resonance – VIPER). The EXSY time window, previously limited by vibrational relaxation (arrow *B*), can thus be extended by multiple orders of magnitude (i.e. to electronic lifetimes). In case the molecule is permanently changed (e.g. it isomerizes) due to the UV/Vis excitation, exchange can even be followed up to “infinite” times.

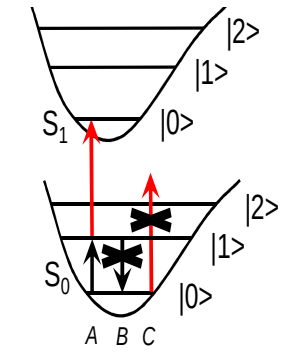

Fig. 1 Energy level scheme showing that information on IR excitation (black) is stored in the electronic excited state by applying a non-resonant UV/VIS pulse (red).

Moreover, sub-ensembles within a mixture of strongly overlapping UV/VIS spectra (e.g. hydrogen bonded vs. non-bonded molecules, different conformers or complexes) can be selected by the infrared pulse and subsequently electronically excited. This opens new possibilities in photophysics and photochemistry, as different reaction pathways and dynamics of coexisting conformers, isomers or species involved in different interactions can be revealed. We illustrate the technique by tracking hydrogen bond formation and dissociation between the laser dye coumarin 6 and methanol over more than hundred picoseconds where the vibrational life time is only 1 ps.

References:

[1] S. Woutersen, Y. Mu, G. Stock, P. Hamm, Chem. Phys. **266** 2-3 (2001) 137-147.

Time resolved IR spectroscopy on the excited state decay in single stranded DNA

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UV-excitation of DNA is known to induce severe damage[1,2] to genetic material. Whereas photophysics and photochemistry of single nucleic acids are well characterized, an understanding of these processes in oligonucleotides is still incomplete.
In our investigation we address transfer processes after UV excitation of oligonucleotides by mid-IR spectroscopy on the picosecond time scale. We use a model system containing three different natural bases, where we excite one base selectively with UV light and probe neighboring bases vibrational marker bands. Excited oligonucleotides with different lengths and sequences are investigated with this method. The measurements show the appearance of long living (100 ps) excited states in oligonucleotides in contrast to much faster processes (< few ps) in single nucleotides. The occurrence of these long living states correlates with the stacking properties and thus depends on the sequence of the DNA. Furthermore characteristic transient absorption bands are found, which indicate the occurrence of charge transfer states. The experimental results indicate a delocalization of these states along the strand over several stacked bases. The investigation shows that UV absorption in DNA results in charge separation and delocalization which is strongly influenced by the stacking properties.

References:
[1] W. J. Schreier et al., *Science*, **315**, 625, 2007
[2] J. S. Taylor, *Acc. Chem. Res*, **27**, 76, 1994

PB32

Determining in situ protein conformation and orientation from the amide-I sum-frequency generation spectrum: theory and experiment

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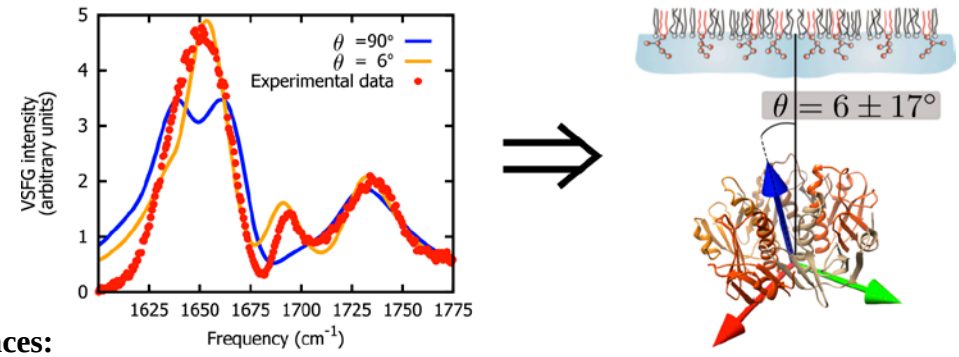
Amide-I vibrational sum-frequency generation (VSFG) spectra of proteins can provide detailed insight into biomolecular processes in and near membranes. However, interpreting these spectra in terms of structure and orientation can be difficult, especially in the case of complex proteins. Here, we present a formalism for calculating the IR, Raman and VSFG spectra of a protein based on its conformation. We set up an amide-I exciton Hamiltonian for the protein backbone amide moieties that generate the spectroscopic responses. To determine the nearest-neighbor couplings we use a B3LYP-calculated map of the coupling as a function of the dihedral angles [1]. The other couplings are estimated using the transition-dipole coupling model [2]. The local-mode frequencies are determined from the number and length(s) of intra- and intermolecular hydrogen bonds, as obtained from MD simulations. From the Hamiltonian we obtain the amide-I normal modes of the protein, from which we calculate the linear and nonlinear spectra.

As a first application, we measure and calculate the VSFG spectra of the cholera toxin B-subunit (515 amino acids) docked to an artificial cell membrane. From the peak ratio in the VSFG spectra obtained with the SSP (SF, Raman & IR, respectively) polarization combination, we determine orientation of the protein with respect to the membrane surface.



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Effect of specific interaction on C=O vibrational dynamics of the excited state 4-Aminopthalimide

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4-Aminopthalimide (4-AP, Fig.1) is often used as a fluorescence probe to study complex media, because of the strong dependence of 4-AP electronic spectra on the properties of its surroundings[1]. 4-AP contains both electron donor and accepter moiety in the structure, forming the hydrogen bonds with various solvent molecules in polar solvents. The photophysical properties of 4-AP studied previously and concluded that the formation of hydrogen bonding complex between 4-AP and solvents stabilized the excited state 4-AP leading the significantly large electronic spectral shift deviating from Lipperd-Mataga polarity $f(\varepsilon, n^2)$ and the quenching of fluorescence lifetimes[1-3]. In our present study, the steady state symmetric and anti-symmetric C=O stretching modes, appeared about 1750 and 1700-1730 cm^{-1} respectively, also showed large solvent dependent spectral shift (Fig. 2). We are currently examining the C=O vibrational dynamics of the excited state 4-AP in aprotic and protic solvents using sub-picosecond time-resolved visible-pump IR-probe spectroscopy. DFT and TDDFT calculations also performed for electronic structure and infrared modes in the ground state and the excited state 4-AP molecule.

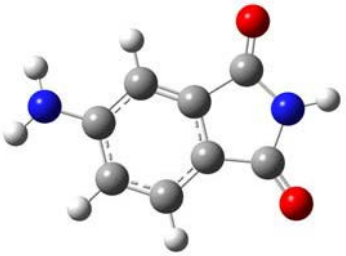

Fig. 1 4-Aminopthalimide

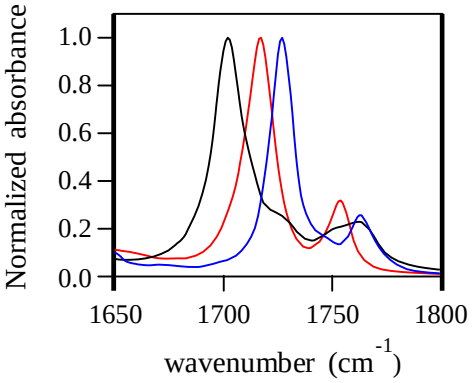

Fig. 2 Steady state IR spectra of 4-AP in methanol (black), dimethyl sulfoxide (red) and acetonitrile (blue).

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Comparison of vibrational dynamics between hydrophobic probe and ionic probe in water studied by two-dimensional infrared spectroscopy

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It is well known that in aqueous solutions hydration structures around hydrophilic and hydrophobic groups are different. Such differences are considered to be important in biological processes and chemical reactions. It is also expected that vibrational dynamics of solute molecule is different on these two cases. In the present study, we use 2-nitro-5-thiocyanatobenzoic acid (NTBA) as a hydrophobic probe. We focus on thiocynate group (-SCN), and examined the effect of hydrophobicity on the vibrational dynamics of solute by two-dimensional infrared (2DIR) spectroscopy.

The obtained 2DIR spectrum and CLS are shown in Figure 1 and Figure 2, respectively. The center line slope (CLS) of the 2DIR signal is plotted against the population time *T*. The CLS can be fitted by a single-exponential function ($\Delta_1^2 exp(-t/\tau) + \Delta_0^2$). The frequency-frequency time correlation function (FFTCF) of ionic probes such as SCN^- was reported in the previous studies [1]. For SCN^- , the FFTCF is expressed by a biexponential function ($\Delta_1^2 exp(-t/\tau_1) + \Delta_2^2 exp(-t/\tau_2)$) with the value of Δ_0 of 0 ps^{-1} and the value of τ_2 of 1.3 ps. On the other hand, in the case of NTBA, the value of Δ_0 is approximately 0.15 ps^{-1} and that of τ is 0.71 ps. Considering these results of the value of Δ_0 and τ, the vibrational dynamics of hydrophobic probe is different from that of hydrophilic probe. It can be thought that the value of Δ_0 and τ of NTBA reflects the existence of faster solvent dynamics around NTBA than SCN^- and slow dynamics which proceeds over more than 2 ps around NTBA.

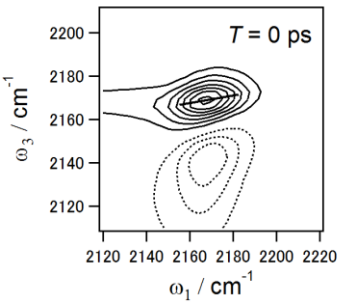

Figure 1. The 2DIR spectrum of NTBA at *T* = 0 ps. Solid and dotted line indicate positive and negative amplitude, respectively. The black line in the spectrum is centre line of the spectrum.

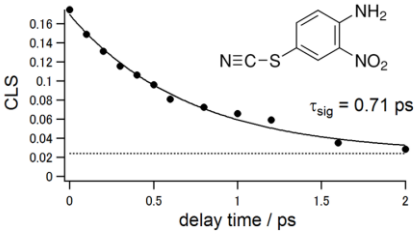

Figure 2. The CLS curve from each 2DIR spectra of NTBA plotted against the population time *T*. The molecule used in this study is shown in the figure.

References:

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PB35

Structure and Dynamics of Aqueous Hydroxides Studied Using Ultrafast Broadband Infrared Spectroscopy

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Anomalously fast diffusion of OH^- ions in water is thought to occur by proton transport (PT) rather than the physical translocation of OH^- ions. As such there are many outstanding questions regarding the role of water's ultrafast hydrogen bond dynamics in proton transfer from water to OH^- ion. To investigate these dynamics we performed ultrafast infrared spectroscopy of aqueous NaOH solutions. On addition of NaOH in H_2O, a broad featureless continuum grows on the lower frequency side of the O—H stretch main band of H_2O, spanning the entire mid-IR region of linear FTIR spectra. Coupled O—H stretch vibrations of first solvation shell water molecules solvating an OH^- ion contribute to this feature.[1] But, to fully understand the origin of such a broad continuum, it is important to understand the dynamics of PT that contribute to it. We performed magic angle pump-probe experiments on NaOH in H_2O with a sub-45 fs pump pulse centered at 2900-3400 cm^{-1} and probed the entire mid-IR region with an ultrafast broadband IR pulse between 1350-4000 cm^{-1}.[2] On addition of NaOH in H_2O, the spectra show a broad bleach in ~2000-3000 cm^{-1} region and a broad induced absorption at <2000 cm^{-1} region, which decay on a very fast timescale of 120-140 fs. To interpret these features, we performed Instantaneous Normal Mode (INM) analysis of the solvated OH^- clusters obtained from a MS-EVB MD simulation. These calculations show how different solvation shell structures contribute to the spectrum. We decompose the collective vibrations of the shell by hydrogen bond coordination number and vibrational symmetry. We find that vibrational frequencies do not correlate well with either coordination number or any particular geometric parameter of the solvated OH^- ion. Therefore, a more collective coordinate like solvent polarization fluctuations are likely to be determining factors in aqueous OH^- solution.

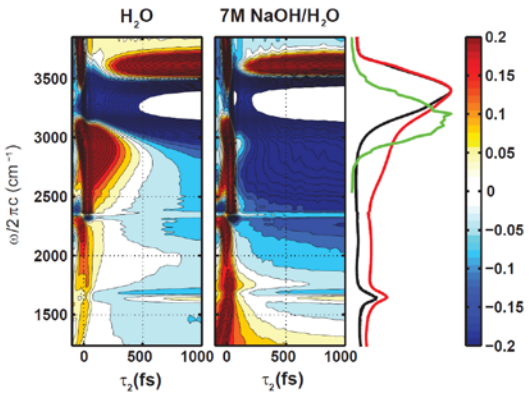

Figure 1*: *MA pump-probe spectra of NaOH in H_2O

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Ultrafast two-dimensional phase-resolved vibrational sum frequency spectroscopy of aqueous interfaces

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Aqueous interfaces are omnipresent in nature and are relevant in physical, chemical, as well as biological fields of research. Thanks to its interface selectivity, vibrational sum-frequency (VSF) spectroscopy is a powerful tool to investigate the structure and orientation of interfacial water molecules through the interfacial, complex non-linear optical response function $\chi^{(2)}$. Recently, ultrafast dynamics of aqueous interfaces have been studied by time-resolved VSF spectroscopy, which provides rich information about energy transfer and reorientational motion at interfaces. To obtain more detailed insight into vibrational and structural dynamics of interfaces, phase-resolved (also known as heterodyne-detected) time-resolved VSF spectroscopy is desired, as first shown by the Tahara group. With this approach time-dependent $\mathrm{Im}[\chi^{(2)}]$ spectra are obtained, which provide direct information on vibrational anharmonicity, spectral diffusion, and inhomogeneity of aqueous interfaces, as opposed to the $|\chi^{(2)}|^2$ spectra obtained with conventional time-resolved VSF spectroscopy.

We report the development of a two-dimensional (2D) heterodyne-detected VSF spectroscopy system, which can be applied to aqueous interfaces. Figure 1 shows a schematic of our 2D heterodyne-detected VSF setup. A local oscillator is generated at a gold surface, followed by the VSF signal generation at the sample. From the interference between the local oscillator and the VSF signal the $\mathrm{Im}[\chi^{(2)}]$ spectra are obtained from which the orientation of the water molecules can be extracted. By exciting the water surface with a high intensity IR pump beam and following the system in time, the energy coupling and vibrational relaxation of these molecules can be revealed. We will present details of the experimental setup and show some first results.

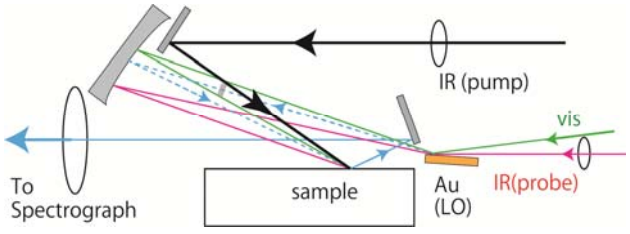

Fig. 1. Schematic of the 2D heterodyne-detected SFG spectroscopic system

Ab Initio Study of $S_3 \rightarrow S_2$ and $S_2 \rightarrow S_1$ internal conversion of PRODAN molecule.

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PRODAN is a fluorescent molecule whose intramolecular charge transfer (ICT) state is relevant for fluorescence. Whether the emitting structure is planar or twisted has long been discussed. Recent theoretical calculation with SAC-CI method showed that planar structure is energetically favorable[1, 2] and is likely to be the emitting state. In Ref. [2], they also reported that the absorption oscillator strength of third excited (S_3) state is larger than that of first excited (S_1) state, and they suggested that possible internal conversion from S_3 to S_2 and from S_2 to S_1 might contribute to the complexity of photophysical phenomena of PRODAN.

We performed geometry optimization of ground state stable structure and S_3/S_2 and S_2/S_1 conical intersection (*ci*) with CIS/6-31G* level of calculation for a PRODAN model molecule (Fig. 1). The energy of S_3/S_2 *ci* is smaller than that of S_3 vertical excitation energy. The energy of S_3/S_2 *ci* is larger than that of S_2/S_1 *ci*. These results imply the possibility of ultrafast internal conversion process from S_3 state to S_1 state. We are going to perform computation with higher level of theory to confirm this. Also we are planning to perform *ab initio* molecular dynamics including non-adiabatic transition in order to simulate the internal conversion process.

		molecular structure		
		gs	*ci* (2-1)	*ci* (3-2)
energy/eV	S0	0.00	0.27	0.19
	S1	5.03	5.06	5.09
	S2	5.13	5.06	5.13
	S3	5.23	5.37	5.13

Table 1. Total energy for each excited state with ground state equilibrium structure (*gs*) and conical intersection (*ci*) between S_2 and S_1 , S_3 and S_2.

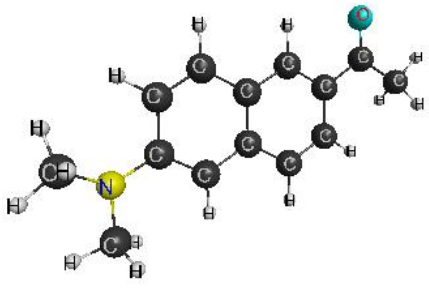

Figure 1. Molecular structure of model molecule for PRODAN. Ethyl group of PRODAN is substituted with methyl group.

References: [1] B. Mennucci *et al.*, *J. Phys. Chem. B*, **112**, 414-423(2008).
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Electrocyclization reaction of a photocromic molecular switch and excited state dynamics of the molecular constituents studied by Femtosecond Stimulated Resonance Raman Scattering

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Transient Raman spectroscopy is an invaluable tool for observing the structural changes that are embedded in the vibrational spectrum of a reacting molecule. This signature is particularly interesting when associated with the rapid rearrangement following a photochemical reaction by means of pump-probe experiments. In recent years the field has been enriched with a new time resolved vibrational probe which allowed going beyond the intrinsic limits of the well established Time Resolved Resonance Raman (TR^3) approach. Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful method for studying chemical and biochemical reaction dynamics driven by short laser pulses, in which the simultaneous presence of two electric fields stimulates the Raman transitionsUsing dispersed detection, the spectral resolution is fundamentally limited by only the evolution and dephasing of an induced vibrational coherence, whereas the time resolution in principle only depends on the duration of the laser pulses that initiate the photochemical reaction (actinic pump) and the vibrational coherence itself (Raman probe). This "disentanglement" of time and energy resolution (approaching 30fs and $15cm^{-1}$, respectively) reveals a more precise picture of the vibrational dynamics than traditional transient vibrational spectroscopy techniques.

Achieving high time and frequency resolution simultaneously is essential for probing the fundamental details of non-adiabatic transitions in photochemical reactions. The compound we present here is an ideal model system for studying non-adiabatic dynamics because of the favorable optical properties and rapid, reversible reactions. Transient absorption measurements of the electrocyclization (ring-closing) reaction are complicated by competing signals from multiple conformations in solution. The tunability of our setup [1] easily allows having the Raman Pump resonant with the electronic absorption bands of the different photoproducts so being able to preferentially catch the dynamics associated with the rapid, sub-picosecond electrocyclization reaction. We find that the nuclear dynamics are substantially slower than the electronic dynamics for the ring-closing reaction. The electronic configuration resembles the product state after only ~100fs, but the nuclear dynamics span a range of tens of picoseconds as the structure of the molecule evolves. Complementary measurements probe the nuclear dynamics of the individual monomers that make up the two sides of the photoswitch, including ultrafast structural relaxation of the singlet excited state as well as picosecond-scale intersystem crossing. The dynamics of the monomer provide insight on the behavior of non-reactive conformers of the photoswitch that do not undergo electrocyclization.

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2D IR spectroscopy with a phase-locked pulse pair delayed by a birefringent delay line

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We present a simple optical arrangement that produces phase-locked pulse pairs for 2D IR spectroscopy in the pump-probe geometry [1,2]. The set up employs three sequences of birefringent lithium niobate blocks cut along different axes (X, Y or Z, corresponding to the orientation of the extraordinary axis, see Fig.1). When propagating through the X or Y-cut blocks, the ordinary and extraordinary polarizations acquire a relative delay depending on the thickness of the material. By moving the Y-cut wedge, this delay can be tuned precisely and used to scan coherence time in a two dimensional spectroscopy experiment in the time domain. The additional wedges are used for maintaining one of the two pulses with a constant delay, correct for the spatial phase and compensate to the first order the group delay dispersion, allowing this device to handle broadband pulses. This principle has already been successfully applied in the visible range [3] and is here demonstrated for the first time in the mid-IR range. We present here our results and will discuss the advantages and drawbacks of this configuration for 2D IR spectroscopy.

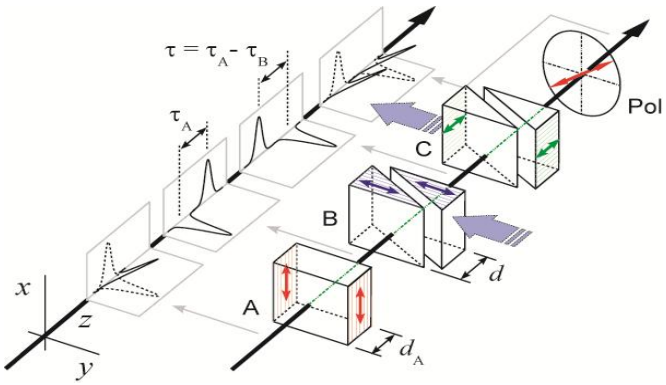

Fig. 1 : Wedge sequence used for generation of phase locked pulse pair. Arrows on blocks indicate the extraordinary axes (adapted from [3]).

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Structural change and ligand discrimination of oxygen sensor protein FixL studied by ultraviolet resonance Raman spectroscopy

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FixL is a heme-based O_2 sensor protein, which responds to low O_2 concentration by activating the transcriptional activator FixJ. Signal transduction is initiated by the dissociation of O_2 from the sensor domain of FixL, resulting in protein conformational changes that are transmitted to a histidine kinase domain. To gain insight into the FixL sensing mechanism, we monitored changes in the protein's structure upon the dissociation of the ligand using ultraviolet resonance Raman (UVRR) spectroscopy.

Observed UVRR spectra contain Y1, Y7a, Y7b, and Y8a bands due to Tyr residues in addition to F1 band due to Phe residues. The Y8a band exhibited to intensity decrease upon ligand dissociation both for O_2 and CO. The intensity decrease of the Y8a band was larger for the O_2 dissociation than for CO dissociation. This implies that structural changes upon the O_2 dissociation are different from those upon CO dissociation and would be associated with the ligand discrimination of FixL. To identify the Tyr residue(s) exhibiting the intensity decrease, we compared UVRR spectra of FixL mutants to those of wild type FixL. Most striking difference was observed in the Y8a band for Y201F mutant, suggesting that a part around Tyr201 undergoes large structural changes upon the O_2 dissociation. We also studied the structural changes of sensor domain sample of FixL upon the ligand dissociation. Ligand-dependent spectral changes were observed similar to those of the full length protein. To elucidate structural dynamics of FixL, we performed time-resolved UVRR measurements on the sensor domain sample. The Y8a band exhibited intensity decrease with a time constant of about 0.2 μs. The signal transduction and ligand discrimination are discussed based on the observed spectra.

References:

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N−H Stretching Excitations in Adenosine-Thymidine Base Pairs in Solution: Pair Geometries, Infrared Line Shapes, and Ultrafast Vibrational Dynamics

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We explore the N-H stretching vibrations of adenosine-thymidine base pairs in chloroform solution with linear and nonlinear infrared spectroscopy [1,2]. Based on estimates from NMR measurements [3] and ab initio calculations, we conclude that adenosine and thymidine form hydrogen bonded base pairs in Watson-Crick, reverse Watson-Crick, Hoogsteen and reverse Hoogsteen configurations with similar probability. Steady-state concentration- and temperature dependent linear FT-IR studies, including H/D exchange experiments, reveal that these hydrogen-bonded base pairs have complex N-H/N-D stretching spectra with a multitude of spectral components. Nonlinear 2D-IR spectroscopic results, together with IR-pump-IR-probe measurements, as also corroborated by ab initio calculations, reveal that the number of N-H stretching transitions is larger than the total number of N-H stretching modes. This is explained by couplings to other modes, such as an underdamped low-frequency hydrogen-bond mode, and a Fermi resonance with NH_2 bending overtone levels of the adenosine amino-group. Our results demonstrate that modeling based on local N-H stretching vibrations only is not sufficient and call for further refinement of the description of the N-H stretching manifolds of nucleic acid base pairs of adenosine and thymidine, incorporating a multitude of couplings with fingerprint and low-frequency modes.

References:

[1] C. Greve, *et al.*, J. Phys. Chem. A **1156** (2012) 7636.

[2] C. Greve, *et al.*, J. Phys. Chem. A **117** (2013) 594.

[3] B. Koeppe, *et al.*, Z. Phys. Chem. (2013) submitted.

Molecular dynamics of proteins in solutions studied by ultrafast Optical Kerr effect (OKE) spectroscopy

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It is well known that biomolecular processes are intimately linked to solvent modes and hence the dynamics and structure of the aqueous solution. However, characterizing the coupled biomolecule-water dynamics is challenging due to the complexity of the system and the wide range in time/frequency of these dynamics. Dielectric-based observation (DRS, time-domain terahertz, IR/FIR absorption) is compromised by absorption, due to the strong dipole moment of water, as well as the limited range of each technique.

Optical Kerr effect spectroscopy (OKE) can however measure a continuous spectrum covering the whole intermolecular region including the low-frequency diffusive relaxations in normal liquids [1,2]. Here we will present OKE studies of small globular proteins (lysozyme, trypsin, lactoglobulin, *etc*.) showing that current high-dynamic-range OKE spectra can reveal strongly characteristic bandshapes (Fig. 1) and reveal previously unobserved dynamics in the picosecond to nanosecond range. OKE experiments were carried out on enzyme–inhibitor complexes that revealed an underdamped mode at *ca*. 2.5 THz associated with the complex. This novel mode will be interpreted through density-of-states calculations and we will discuss its role in quantum mechanical effects in biomolecular reactivity.

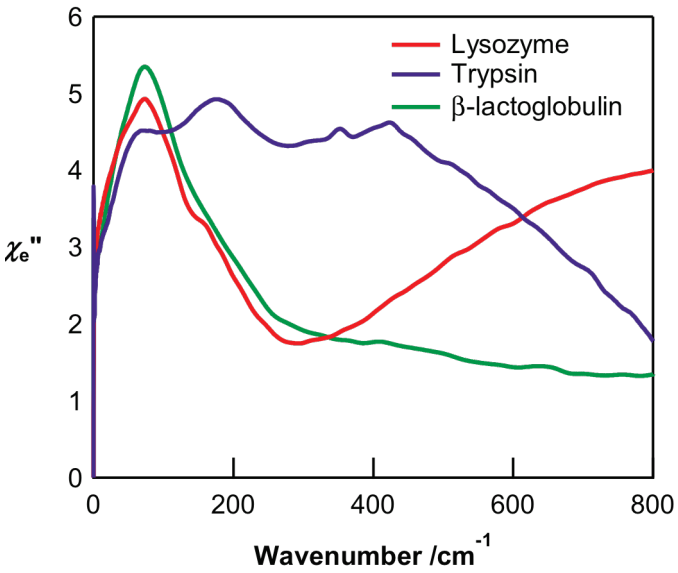

Fig. 1 Imaginary part of the OKE spectrum for lysozyme, trypsin, and β-lactoglobulin.

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[1] G. Giraud, J. Karolin, and K. Wynne, Biophys. J. **85** (2003) 1903.

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Vibrational relaxation dynamics of the pseudohalide (PS) complexes $Ru(bpy)_2(PS)_2$, PS = CN, NCS and N_3

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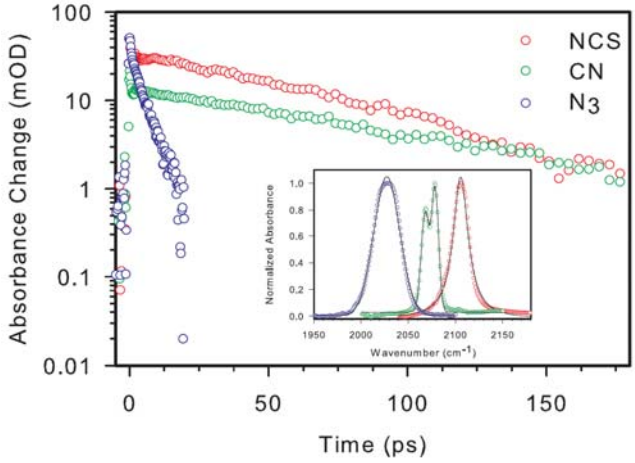
Static and transient infrared (IR) spectroscopy were used to investigate *cis*-$Ru(bpy)_2(N_3)_2$ (bpy = 2,2'-bipyridine), *cis*-$Ru(bpy)_2(NCS)_2$, and *cis*-$Ru(bpy)_2(CN)_2$ in solution. The CN-stretching IR band for *cis*-$Ru(bpy)_2(NCS)_2$ appears at higher frequency (~2106 cm^{-1} in DMSO) than for the free NCS^- anion while the IR bands for the azide and cyanide complexes are closer to those of the respective free anions. The vibrational energy relaxation (VER) lifetime for the azide complex is found to be much shorter (~ 5 ps) than for either the NCS or CN species (both ~ 70 ps in DMSO) and the lifetimes resemble those for each corresponding free anion in solution. However, for *cis*-$Ru(bpy)_2(N_3)_2$, the transition frequency depends more on the solvent than the VER lifetime implying that intramolecular vibrational relaxation (IVR) is predominant over solvent energy-extracting interactions. These results will also be compared to the behavior of other related metal complexes in solution.



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